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DEVELOPMENT DOCUMENT FOR EFFLUENT LIMITATIONS GUIDELINES AND NEW SOURCE PERFORMANCE STANDARDS FOR THE PETROLEUM REFINING POINT SOURCE CATEGORY

ENVIRONMENTAL PROTECTION AGENCY

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This development document presents the findings of an extensive study of the Petroleum Refining Industry for the purposes of developing effluent limitation guidelines, standards of performance, and pretreatment standards for the industry to implement Sections 304, 306, and 307 of the Federal Water Pollution Control Act of 1972, (PL 92-500). Guidelines and standards were developed for the overall petroleum refining industry, which was divided into five subcategories.

Effluent limitation guidelines contained herein set forth the degree of reduction of pollutants in effluents that is attainable through the application of best practicable control technology currently available (BPCTCA), and the degree of reduction attainable through the application of best available technology economically achievable (BATEA) by existing point sources for July 1, 1977, and July 1, 1983, respectively. Standards of performance for new sources are based on the application of best available demonstrated technology (BADT).

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DEVELOPMENT DOCUMENT
for
EFFLUENT LIMITATIONS GUIDELINES
and
NEW SOURCE PERFORMANCE STANDARDS
for the
PETROLEUM REFINING POINT SOURCE CATEGORY

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ABSTRACT

This development document presents the findings of an extensive study of the Petroleum Refining Industry for the purposes of developing effluent limitation guidelines, standards of performance, and pretreatment standards for the industry to implement Sections 304, 306 and 307 of the Federal Water Pollution Control Act of 1972, (PL 92-500). Guidelines and standards were developed for the overall petroleum refining industry, which was divided into five subcategories.

Effluent limitation guidelines contained herein set forth the degree of reduction of pollutants in effluents that is attainable through the application of best practicable control technology currently available (BPCTCA), and the degree of reduction attainable through the application of best available technology economically achievable (BATEA) by existing point sources for July 1, 1977, and July 1, 1983, respectively. Standards of performance for new sources are based on the application of best available demonstrated technology (BADT).

Annual costs for the petroleum refining industry for achieving BPCTCA Control by 1977 are estimated at $244,000,000, and the additional annual costs for attaining BATEA Control by 1980 are estimated at $250,000,000. The estimated annual costs for BADT for new sources is $26,000,000.

Supporting data and rationale for the development of proposed effluent limitation guidelines and standards of performance are contained in this development document.

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SECTION I

CONCLUSIONS

This study covered the products included in the Petroleum Refining Industry (SIC 2911). The 252 U.S. petroleum refineries currently process 2.2 million cubic meters (14 million barrels) of crude oil per stream day. U.S. refineries vary in complexity from the very small, with simple atmospheric fractionation, or topping, to the very large integrated refineries manufacturing a multitude of petroleum and petrochemical products from a variety of feedstocks. The raw waste water load is dependent upon the types of processes employed by the refinery, justifying the utilization of production process groupings, as delineated by their effects on raw waste water as the basis for the subcategorization. The subcategories developed for the petroleum refining industry for the purpose of establishing effluent limitations are as follows:

Subcategory	Basic Refinery Operations Included
Topping	Topping, catalytic reforming, asphalt production, or lube oil manufacturing processes, but excluding any facility with cracking or thermal operations.
Cracking	Topping and cracking.
Petrochemical	Topping, cracking and petrochemicals operations.*
Lube	Topping, cracking and lube oil manufacturing processes.
Integrated	Topping, cracking, lube oil manufacturing processes and petrochemicals operations.*

* The term "petrochemical operations" shall mean the production of second generation petrochemicals (i.e. alcohols, ketones, cumene, styrene, etc.) or first generation petrochemicals and isomerization products (i.e. BTX, olefins, cyclohexane, etc.) when 15% or more of refinery production is as first generation petrochemicals and isomerization products.

All five subcategories generate waste waters which contain similar constituents. However, the concentration and loading of these constituents, termed "raw waste load," vary between the subcategories. Existing control and treatment technology, as practiced by the industry, includes both end-of-pipe treatment and in-plant reductions. Many of the individual wastewater streams, such as sour waters, have a deleterious effect on biological treatment facilities and/or receiving waters. Consequently, these individual streams are pretreated in-plant, prior to discharge to waste water facilities. Current technology for end-of-pipe treatment involves biological treatment and granular media filtration. Biological treatment systems employed include activitated sludge plants and aerated lagoons and stabilization pond systems.

SECTION II

RECOMMENDATIONS

The significant waste water constituents are BOD_5, COD, TOC, total suspended solids, oil and grease, phenolic compounds, ammonia (N), sulfides, total and hexavalent chromium. These waste water constituents were selected to be the subject of the effluent limitations.

Effluent limitations commensurate with the best practical control technology currently available are proposed for each refinery subcategory. These limitations, listed in Tables 1-6 are explicit numerical values for the allowable discharges within each subcategory. Implicit in BPCTCA in-process technology is segregation of non-contact waste waters from process waste water. BPCTCA end-of-pipe technology is based on the application of the existing waste water treatment processes currently used in the Petroleum Refining Industry. These consist of equilization and storm diversion; initial oil and solids removal (API separators or baffle plate separators); further oil and solids removal (clarifiers, dissolved air flotation, or filters); carbonaceous waste removal (activated sludge, aerated lagoons, oxidation ponds, trickling filter, activated carbon, or combinations of these); and filters (sand, dual media; or multi-media) following biological treatment methods. The variability of performance of biological waste water treatment systems has been recognized in the development of the BPCTCA effluent limitations.

Effluent limitations commensurate with the best available technology economically achievable are proposed for each subcategory. These effluent limitations are listed in Tables 1-6. The limitations are explicit numerical values for the allowable discharges within each subcategory. The primary end-of-pipe treatment proposed for BATEA effluent limitations is activated carbon adsorption, as further treatment in addition to BPCTCA control technology. Also implicit in BATEA technology are achievable reductions in waste water flow.

New source performance standards commensurate with the best available demonstrated technology are based on the flows achievable with BATEA technology, and the end-of-pipe control technology achievable with BPCTCA technology. These BADT effluent limitations are listed in Tables 1-6. Activated carbon adsorption has not been included as BADT technology, since the use of this technology has not been sufficiently demonstrated, at this time, on petroleum refining waste water to insure its applicability and reliability on secondary effluent waste waters from refineries.

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Table 1
Petroleum Refining Industry Effluent Limitations
Topping Subcategory

	BPCTCA Effluent limitations (a)(b)		BATEA Effluent limitations (a)(b)		BADT Effluent limitations (a)(b)	
	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed
(Metric units)	kg/k cu m of feedstock		kg/k cu m of feedstock		kg/k cu m of feedstock	
BOD5	22.7	12.0	2.5	2.0	11.8	6.3
TSS	13.9	8.2	2.4	2.0	7.3	4.0
COD	117	60.3	10.0	8.0	61	32
Oil and grease	6.9	3.7	0.50	0.40	3.6	1.9
Phenolic compounds	0.168	0.076	0.012	0.0090	0.088	0.043
Ammonia as N	2.81	1.27	0.68	0.51	2.8	1.3
Sulfide	0.149	0.068	0.055	0.035	0.078	0.035
Total chromium	0.345	0.20	0.124	0.105	0.18	0.105
Hexavalent chromium	0.0071	0.0031	0.0026	0.0017	0.0037	0.0017
pH	Within the range 6.0 to 9.0		Within the range 6.0 to 9.0		Within the range 6.0 to 9.0	
(English units)	lb/Mbbl of feedstock		lb/Mbbl of feedstock		lb/Mbbl of feedstock	
BOD5	8.0	4.25	0.92	0.75	4.2	2.2
TSS	4.9	2.9	0.88	0.75	2.6	1.5
COD	41.2	21.3	3.5	2.8	21.7	11.2
Oil and grease	2.5	1.3	0.18	0.14	1.3	0.70
Phenolic compounds	0.060	0.027	0.0043	0.0031	0.031	0.016
Ammonia as N	0.99	0.45	0.24	0.18	1.0	0.45
Sulfide	0.053	0.024	0.019	0.015	0.027	0.012
Total chromium	0.122	0.071	0.044	0.037	0.064	0.037
Hexavalent chromium	0.0025	0.0011	0.00097	0.00062	0.0013	0 00062
pH	Within the range 6.0 to 9.0		Within the range 6.0 to 9.0		Within the range 6.0 to 9.0	

(a) The limits set forth above are to be multiplied by the following factors to arrive at the maximum for any one day and the maximum average of daily values for thirty consecutive days.

(1) Size factor

Mbbl of feedstock per stream day	Size factor
0 - 49.9	1.02
50 - 99.9	1.21
100 -149.9	1.44
150 or greater	1.57

(2) Process factor

Process configuration	Process factor
1.0 - 3.99	0.60
4.0 - 6.99	1.00
7.0 - 9.99	1.66
10.0 - 12.99	2.77
13.0 - 15.0 or greater	4.09

(b) The additional allocations to be applied where appropiate for storm water runoff and ballast water are in Table 6.

Table 2
Petroleum Refining Industry Effluent Limitations
Cracking Subcategory

	BPCTCA Effluent limitations (a)(b)		BATEA Effluent limitations (a)(b)		BADT Effluent limitations (a)(b)	
	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed
(Metric units)	kg/k cu m of feedstock		kg/k cu m of feedstock		kg/k cu m of feedstock	
BOD5	28.2	15.6	3.4	2.7	16.3	8.7
TSS	17.1	10.2	3.2	2.7	9.9	5.8
COD[3]	210	109	19.2	15.4	118	61
Oil and grease	8.4	4.5	0.68	0.54	4.8	2.6
Phenolic compounds	0.21	0.10	0.016	0.011	0.119	0.058
Ammonia as N	18.8	8.5	4.6	3.5	18.8	8.6
Sulfide	0.18	0.082	0.075	0.048	0.105	0.048
Total chromium	0.43	0.25	0.16	0.14	0.24	0.14
Hexavalent chromium	0.0087	0.0040	0.0035	0.0022	0.0050	0.0022
pH	Within the range 6.0 to 9.0		Within the range 6.0 to 9.0		Within the range 6.0 to 9.0	
(English units)	lb/Mbbl of feedstock		lb/Mbbl of feedstock		lb/Mbbl of feedstock	
BOD5	9.9	5.5	1.2	0.99	5.8	3.1
TSS	6.1	3.6	1.2	0.99	3.5	2.0
COD[3]	74	38.4	6.8	5.4	41.5	21
Oil and grease	3.0	1.6	0.24	0.19	1.7	0.93
Phenolic compounds	0.074	0.036	0.0055	0.0039	0.042	0.020
Ammonia as N	6.6	3.0	1.6	1.2	6.6	3.0
Sulfide	0.065	0.029	0.026	0.017	0.037	0.017
Total chromium	0.15	0.088	0.058	0.049	0.084	0.049
Hexavalent chromium	0.0031	0.0014	0.0013	0.0008	0.0018	0.00081
pH	Within the range 6.0 to 9.0		Within the range 6.0 to 9.0		Within the range 6.0 to 9.0	

(a) The limits set forth above are to be multiplied by the following factors to arrive at the maximum for any one day and the maximum average of daily values for thirty consecutive days.

(1) Size factor

Mbbl of feedstock per stream day	Size factor
0 - 34.9	0.89
35 - 74.9	1.00
75 - 109.9	1.14
110 - 149.9	1.31
150 or greater	1.41

(2) Process factor

Process configuration	Process factor
1.5 - 3.49	0.58
3.50 - 5.49	0.81
5.50 - 7.49	1.13
7.50 - 9.49	1.60
9.50 - 10.5 or greater	1.87

(b) The additional allocations to be applied where appropiate for storm water runoff and ballast water are in Table 6.

Table 3
Petroleum Refining Industry Effluent Limitations
Petrochemical Subcategory

	BPCTCA Effluent limitations (a)(b)		BATEA Effluent limitations (a)(b)		BADT Effluent limitations (a)(b)	
	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed
(Metric units)	kg/k cu m of feedstock		kg/k cu m of feedstock		kg/k cu m of feedstock	
BOD5	34.6	18.4	4.6	3.7	21.8	11.6
TSS	20.6	12.0	4.4	3.7	13.1	7.7
COD*	210	109	22	17	133	69
Oil and grease	11.1	5.9	0.90	0.72	6.6	3.5
Phenolic compounds	0.25	0.120	0.022	0.015	0.158	0.077
Ammonia as N	23.4	10.6	5.6	4.2	23.4	10.7
Sulfide	0.22	0.099	0.099	0.063	0.140	0.063
Total chromium	0.52	0.30	0.22	0.19	0.32	0.19
Hexavalent chromium	0.0115	0.0051	0.0048	0.0031	0.0062	0.0031
pH	Within the range 6.0 to 9.0		Within the range 6.0 to 9.0		Within the range 6.0 to 9.0	
(English units)	lb/Mbbl of feedstock		lb/Mbbl of feedstock		lb/Mbbl of feedstock	
BOD5	12.1	6.5	1.7	1.3	7.7	4.1
TSS	7.3	4.25	1.6	1.3	4.6	2.7
COD*	74	38.4	7.6	6.1	47	24
Oil and grease	3.9	2.1	0.32	0.26	2.4	1.3
Phenolic compounds	0.088	0.0425	0.0077	0.0054	0.056	0.027
Ammonia as N	8.25	3.8	2.0	1.5	8.3	3.8
Sulfide	0.078	0.035	0.035	0.022	0.050	0.022
Total chromium	0.183	0.107	0.080	0.068	0.116	0.068
Hexavalent chromium	0.0040	0.0018	0.0017	0.0011	0.0024	0.0011
pH	Within the range 6.0 to 9.0		Within the range 6.0 to 9.0		Within the range 6.0 to 9.0	

(a) The limits set forth above are to be multiplied by the following factors to arrive at the maximum for any one day and the maximum average of daily values for thirty consecutive days.

(1) Size factor

Mbbl of feedstock per stream day	Size factor
0 - 49.9	0.73
50 - 99.9	0.87
100 - 149.9	1.04
150 or greater	1.13

(2) Process factor

Process configuration	Process factor
3.25 - 4.74	0.67
4.75 - 6.74	0.91
6.75 - 8.74	1.27
8.75 - 10.25 or greater	1.64

(b) The additional allocations to be applied where appropiate for storm water runoff and ballast water are in Table 6.

Table 4
Petroleum Refining Industry Effluent Limitations
Lube Subcategory

	BPCTCA Effluent limitations (a)(b)		BATEA Effluent limitations (a)(b)		BADT Effluent limitations (a)(b)	
	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed
(Metric units)	kg/k cu m of feedstock		kg/k cu m of feedstock		kg/k cu m of feedstock	
BOD5	50.6	25.8	7.8	6.3	34.6	18.4
TSS	31.3	18.4	7.4	6.3	20.6	12.1
COD*	360	187	40	32	245	126
Oil and grease	16.2	8.5	1.4	1.1	10.5	5.6
Phenolic compounds	0.38	0.184	0.034	0.024	0.25	0.12
Ammonia as N	23.4	10.6	5.6	4.2	23.4	10.7
Sulfide	0.33	0.150	0.16	0.10	0.22	0.10
Total chromium	0.77	0.45	0.36	0.31	0.52	0.31
Hexavalent chromium	0.017	0.0076	0.0081	0.0052	0.0115	0.0052
pH	Within the range 6.0 to 9.0		Within the range 6.0 to 9.0		Within the range 6.0 to 9.0	
(English units)	lb/Mbbl of feedstock		lb/Mbbl of feedstock		lb/Mbbl of feedstock	
BOD5	17.9	9.1	2.7	2.2	12.2	6.5
TSS	11.0	6.5	2.6	2.2	7.3	4.3
COD*	127	66	13.8	11.0	87	45
Oil and grease	5.7	3.0	0.50	0.40	3.8	2.0
Phenolic compounds	0.133	0.065	0.012	0.0087	0.088	0.043
Ammonia as N	8.3	3.8	2.0	1.5	8.3	3.8
Sulfide	0.118	0.053	0.055	0.035	0.078	0.035
Total chromium	0.273	0.160	0.13	0.11	0.180	0.105
Hexavalent chromium	0.0059	0.0027	0.0029	0.0018	0.0056	0.0018
pH	Within the range 6.0 to 9.0		Within the range 6.0 to 9.0		Within the range 6.0 to 9.0	

(a) The limits set forth above are to be multiplied by the following factors to arrive at the maximum for any one day and the maximum average of daily values for thirty consecutive days.

(1) Size factor

Mbbl of feedstock per stream day	Size factor
30 - 69.9	0.71
70 - 109.9	0.81
110 - 149.9	0.93
150 - 199.9	1.09
200 or greater	1.19

(2) Process factor

Process configuration	Process factor
6.0 or less - 7.99	0.88
8.0 - 9.99	1.23
10.0 - 11.99	1.74
12.0 - 14.0 or greater	2.44

(b) The additional allocations to be applied where appropiate for storm water runoff and ballast water are in Table 6.

Table 5
Petroleum Refining Industry Effluent Limitations
Integrated Subcategory

	BPCTCA[(a)(b)] Effluent limitations		BATEA[(a)(b)] Effluent limitations		BADT[(a)(b)] Effluent limitations	
	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed
(Metric units)	kg/k cu m of feedstock		kg/k cu m of feedstock		kg/k cu m of feedstock	
BOD5	54.4	28.9	8.8	7.1	41.6	22.1
TSS	32.8	19.2	8.4	7.1	24.7	14.5
COD*	368	198	47	38	295	152
Oil and grease	17.1	9.1	1.7	1.4	12.6	6.7
Phenolic compounds	0.40	0.192	0.041	0.029	0.30	0.14
Ammonia as N	23.4	10.6	5.6	4.2	23.4	10.7
Sulfide	0.35	0.158	0.19	0.12	0.26	0.12
Total chromium	0.82	0.48	0.44	0.37	0.64	0.37
Hexavalent chromium	0.017	0.0079	0.0092	0.0059	0.013	0.0059
pH	Within the range 6.0 to 9.0		Within the range 6.0 to 9.0		Within the range 6.0 to 9.0	
(English units)	lb/Mbbl of feedstock		lb/Mbbl of feedstock		lb/Mbbl of feedstock	
BOD5	19.2	10.2	3.2	2.6	14.7	7.8
TSS	11.6	6.8	3.0	2.6	8.7	5.1
COD*	136	70	16.8	13.4	104	54
Oil and grease	6.0	3.2	0.60	0.48	4.5	2.4
Phenolic compounds	0.14	0.068	0.015	0.010	0.105	0.051
Ammonia as N	8.3	3.8	2.0	1.5	8.3	3.8
Sulfide	0.124	0.056	0.066	0.042	0.093	0.042
Total chromium	0.29	0.17	0.15	0.13	0.220	0.13
Hexavalent chromium	0.0062	0.0028	0.0033	0.0021	0.0047	0.0021
pH	Within the range 6.0 to 9.0		Within the range 6.0 to 9.0		Within the range 6.0 to 9.0	

(a) The limits set forth above are to be multiplied by the following factors to arrive at the maximum for any one day and the maximum average of daily values for thirty consecutive days.

(1) Size factor

Mbbl of feedstock per stream day	Size factor
70 - 144.9	0.69
150 - 219.9	0.89
220 or greater	1.02

(2) Process factor

Process configuration	Process factor
6.0 or less - 7.49	0.78
7.5 - 8.99	1.00
9.0 - 10.5 or greater	1.30

(b) The additional allocations to be applied where appropiate for storm water runoff and ballast water are in Table 6.

Table 6
Petroleum Refining Industry Effluent Limitations
Storm Water Runoff and Ballast Water

Reproduced from best available copy.

a) Runoff: The allocation being allowed for storm runoff flow shall be based solely on that storm flow (process area runoff) which is treated in the main treatment system. All additional storm runoff (from tankfields and non-process areas) that has been segregated from the main waste stream for discharge, shall not exceed a concentration of 35 mg/l of TOC or 15 mg/l of oil and grease when discharged.

	BPCTCA Effluent limitations (a)(b)		BATEA Effluent limitations (a)(b)		BADT Effluent limitations (a)(b)	
	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed
(Metric units)	kg/cu m of flow		kg/cu m of flow		kg/cu m of flow	
BOD5	0.048	0.026	0.0105	0.0085	0.048	0.026
TSS	0.029	0.017	0.010	0.0085	0.029	0.017
COD	0.37	0.19	0.028	0.022	0.37	0.19
Oil and grease	0.015	0.008	0.0020	0.0016	0.015	0.0080
pH	Within the range 6.0 to 9.0		Within the range 6.0 to 9.0		Within the range 6.0 to 9.0	
(English units)	lb/Mgal of flow		lb/Mgal of flow		lb/Mgal of flow	
BOD5	0.40	0.21	0.088	0.071	0.40	0.21
TSS	0.24	0.14	0.084	0.071	0.24	0.14
COD	3.1	1.6	0.24	0.19	3.1	1.6
Oil and grease	0.126	0.067	0.018	0.014	0.126	0.067
pH	Within the range 6.0 to 9.0		Within the range 6.0 to 9.0		Within the range 6.0 to 9.0	

b) Ballast: The allocation being allowed for ballast water flow shall be based on those ballast waters treated at the refinery.

	BPCTCA Effluent limitations (a)(b)		BATEA Effluent limitations (a)(b)		BADT Effluent limitations (a)(b)	
	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed	Maximum for any one day	Average of daily values for thirty consecutive days shall not exceed
(Metric units)	kg/cu m of flow		kg/cu m of flow		kg/cu m of flow	
BOD5	0.048	0.026	0.0105	0.0085	0.048	0.026
TSS	0.029	0.017	0.010	0.0085	0.029	0.017
COD*	0.47	0.24	0.038	0.030	0.47	0.24
Oil and grease	0.015	0.008	0.0020	0.0016	0.015	0.0080
pH	Within the range 6.0 to 9.0		Within the range 6.0 to 9.0		Within the range 6.0 to 9.0	
(English units)	lb/Mgal of flow		lb/Mgal of flow		lb/Mgal of flow	
BOD5	0.40	0.21	0.088	0.071	0.40	0.21
TSS	0.24	0.14	0.084	0.071	0.24	0.14
COD*	3.9	2.0	0.32	0.26	3.9	2.0
Oil and grease	0.126	0.067	0.018	0.014	0.126	0.067
pH	Within the range 6.0 to 9.0		Within the range 6.0 to 9.0		Within the range 6.0 to 9.0	

SECTION III

INTRODUCTION

Purpose and Authority

Section 301(b) of the Act requires the achievement by no later than July 1, 1977, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best practicable control technology currently available as defined by the Administrator, pursuant to section 304(b) of the Act. Section 301(b) also requires the achievement by not later than July 1, 1983, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best available technology economically achievable, which will result in reasonable further progress toward the national goal of eliminating discharge of all pollutants, as determined in accordance with regulations issued by the Administrator, pursuant to section 304(b) of the Act. Section 306 of the Act requires the achievement by new sources of a Federal standard of performance providing for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator determines to be achievable through the application of the best available demonstrated technology, processes, operative methods or other alternatives, including, where practicable, a standard permitting no discharge of pollutants.

Section 304(b) of the Act requires the Administrator to publish within one year of enactment of the Act, regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable through the application of the best control measures and practices achievable including treatment techniques, process and procedure innovations, operation methods and other alternatives. The regulations proposed herein set forth effluent limitations guidelines pursuant to section 304(b) of the Act for the petroleum refining industry source category.

Section 306 of the Act requires the Administrator, within one year after a category of sources is included in a list published pursuant to section 306(b) (1)(A) of the Act, to propose regulations establishing Federal standards of performance for new sources within such categories. The Administrator published in the Federal Register of January 16, 1973 (38 F.R. 1624), a list of 27 source categories. Publication of the list constituted announcement of the Administrator's intention of establishing, under section 306, standards of performance applicable to new sources within the petroleum refining industry source category which was included in the list published January 16, 1973.

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Methods Used for Development of the Effluent Limitations Guidelines and Standards of Performance

The Office of Air and Water Programs of the Environmental Protection Agency has been given the responsibility for the development of effluent limitation guidelines and new source standards as required by the Act. In order to promulgate the required guidelines and standards, the following procedure was adopted.

The point source category was first categorized for the purpose of determining whether separate limitations and standards are appropriate for different segments within a point source category. Such sub-categorization was based upon raw materials used, products produced, manufacturing processes employed, raw waste loads, and other factors. This included an analysis of (1) the source and volume of water used in the plant and the sources of waste and waste waters in the plant; and (2) the constituents (including thermal) of all waste waters (including toxic constituents and other constituents) which result in taste, odor, and color in water or aquatic organisms. The constituents of waste waters which should be subject to effluent limitations guidelines and standards of performance were identified.

The full range of control and treatment technologies existing within each subcategory was identified. This included an identification of each distinct control and treatment technology, including both inplant and end-of-pipe technologies, which are existent or capable of being designed for each subcategory. It also included an identification, in terms of the amount of constituents (including thermal) and the chemical, physical, and biological characteristics of pollutants, of the effluent level resulting from the application of each of the treatment and control technologies. The problems, limitations, and reliability of each treatment and control technology, and the required implementation time was also identified. In addition, the nonwater quality environmental impact (such as the effects of the applisubcation of such technologies upon other pollution problems, including air, solid waste, noise, and radiation) was also identified. The energy requirement of each of the control and treatment technologies was identified, as well as the cost of the application of such technologies.

The information, as outlined above, was then evaluated in order to determine methods or other alternatives. In identifying such technologies, various factors were considered. These included the total cost of application of technology in relation to the effluent reduction benefits to be achieved from such application, the age of equipment and facilities involved, the processes employed, the engineering aspects of the application of various types of control techniques, process changes, nonwater quality environmental impact (including energy requirements) and other factors.

During the initial phases of the study, an assessment was made of the availability, adequacy, and usefulness of all existing data sources. Data on the identity and performance of waste water treatment systems within the petroleum refining industry were known to be included in:

1. National Petroleum Refining Waste Water Characterization Studies and the Petroleum Industry Raw Waste Load Survey of 1972. (EPA/API Raw Waste Load Survey).

2. Environmental Protection Agency (Refuse Act) Permit Application.

3. Self-reporting discharge data from various states.

4. Monitoring data on individual refineries, collected by state agencies and/or regional EPA offices.

A preliminary analysis of these data indicated an obvious need for additional information. Although approximately 135 refineries were surveyed during the 1972 Raw Waste Load Survey, five activated sludge treatment plants were subjected to intensive sampling for identification of waste water treatment plant effluent performance. Identification of the types of treatment facilities used by the other individual refineries included no performance data.

Refuse Act Permit Application data are limited to identification of the treatment systems used and reporting of final concentrations (which were diluted with cooling waters in many cases); consequently, operating performance could not be established.

Self-reporting data was available from Texas, Illinois, and Washington. These reports show only the final effluent concentrations and identify the systems in use; rarely is there production information available which would permit the establishment of unit waste loads.

Monitoring data from the individual states and/or regional EPA offices again show only the final effluent concentrations and identify the systems in use. Rarely is production information available to permit the establishment of unit waste loads.

Additional data in the following areas were therefore required: 1) currently practiced or potential in-process waste control techniques; 2) identity and effectiveness of end-of-pipe waste control techniques; and 3) long-term data to establish the variability of performance of the end-of-pipe waste control techniques. The best source of information was the petroleum refineries themselves. New information was obtained from direct interviews and inspection visits to petroleum refinery facilities. Verification of data relative to long-term performance of waste control techniques was obtained by the use of standard EPA reference samples to determine the reliability of data submitted by the petroleum refineries, and by comparison of the refinery data with monitoring data from the state agencies and/or regional EPA offices.

The selection of petroleum refineries as candidates to be visited was guided by the trial categorization, which was based on the 1972 Raw Waste Load Survey. The final selection was developed from identifying information available in the 1972 Raw Waste Load Survey, EPA Permit Applications, state self-reporting discharge data, and contacts within regional EPA offices and the industry. Every effort was made to choose facilities where meaningful information on both treatment facilities and manufacturing processes could be obtained.

Survey teams composed of project engineers conducted plant visits. Information on the identity and performance of waste water treatment systems were obtained through:

1. Interviews with plant water pollution control personnel.

2. Examinations of treatment plant design and historical data (flow rates and analyses of influent and effluent).

3. Inspection of operations and analytical procedures, including verification of reported analyses by the use of EPA standard reference samples and by comparison of the refinery data with monitoring data from state agencies and/or regional EPA offices.

Information on process plant operations and associated waste water characteristics were obtained through:

1. Interviews with plant operating personnel.

2. Examination of plant design and operating data.

3. Inspection of in-plant waste water controls.

The data base obtained in this manner was then utilized to develop recommended effluent limitations and standards of performance for the petroleum refining industry. All of the references utilized are included in Section XIII of this report. The data obtained during the field data collection program are included in Supplement B.

General Description of the Industry

The industrial waste water profile covers the petroleum refining industry in the United States, as defined by Standard Industrial Classification (SIC) Code 2911 of the U.S. Department of Commerce. Intermediates and finished products in this industry are numerous and varied. Table 7 is a partial listing of these products. The production of crude oil or natural gas from wells, or the production of natural gasoline and other operations

TABLE 7

Intermediates and Finished Products Frequently Found in the Petroleum Refining Industry

SIC 2911

Acid Oil
Alkylates
Aromatic Chemicals
Asphalt and Asphaltic Materials:
  Semi-Solid and Solid
Benzene
Benzol
Butadiene
Coke (Petroleum)
Fuel Oils
Gas, Refinery or Still Oil
Gases, (LPG)
Gasoline, except natural gasoline
Greases: Petroleum, mineral jelly,
  lubricative, etc.
Jet Fuels
Kerosene
Mineral Oils, natural
Mineral Waxes, natural
Naphtha
Naphthenic Acids
Oils, partly refined
Paraffin Wax
Petroleums, nonmedicinal
Road Oils
Solvents
Tar or Residuum

associated with such production, as covered under SIC Code 1311, are not within the scope of this study. This study also does not include distribution activities, such as gasoline service stations. Transportation of petroleum products is covered only to the extent that it is part of refinery pollution control, such as the treatment of ballast water. Other activities outside the scope of the SIC Code 2911 were included in the development of raw waste load data, and are listed as auxiliary processes which are inherent to an integrated refinery operation. Some of these include soap manufacture for the production of greases, steam generation, and hydrogen production.

A petroleum refinery is a complex combination of interdependent operations engaged in the separation of crude molecular constituents, molecular cracking, molecular rebuilding and solvent finishing to produce the products listed under SIC Code 2911. The refining operations may be divided among 12 general categories, where each category defines a group of refinery operations. The categories are listed in Table 8.

The characteristics of the waste water differ considerably for different processes. Considerable knowledge is available that can be used to make meaningful qualitative interpretations of pollutant loadings from refinery processes. Such information is presented in Table 9, a semi-graphic outline of the major sources of pollutants within a refinery. In order to set forth the character of the waste derived from each of the industry categories established in Section IV, it is essential to study the sources and contaminants within the individual production processes and auxiliary activities. Each process is itself a series of unit operations which causes chemical and/or physical changes in the feedstock or products. In the commercial synthesis of a single product from a single feedstock, there generally are sections of the process associated with: the preparation of the feedstock, the chemical reaction, the separation of reaction products, and the final purification of the desired product. Each unit operation may have drastically different water usages associated with it. The type and quantity of contact waste water are therefore directly related to the nature of the various processes. This in turn implies that the types and quantities of waste water generated by each plant's total production mix are unique. The processes and activities along with brief process descriptions, trends in applications, and a delineation of waste water sources, are as follows:

TABLE 8

Major Refinery Process Categories

1. Storage and Transporation
2. Crude Processes
3. Coking Processes
4. Cracking and Thermal Processes
5. Hydrocarbon Processing
6. Petrochemical Operations
7. Lube Manufacturing Processes
8. Treating and Finishing
9. Asphalt Production
10. Auxiliary Activities (Not listed under SIC Code 2911)

TABLE 9

Qualitative Evaluation of Wastewater Flow and Characteristics by Fundamental Refinery Processes

Production Processes	Flow	BOD	COD	Phenol	Sulfide	Oil	Emulsified Oil	pH	Temp.	Ammonia	Chloride	Acidity	Alkalinity	Susp. Solids
Crude Oil and Product Storage	XX	X	XXX	X		XXX	XX	0	0	0		0		XX
Crude Desalting	XX	XX	XX	X	XXX	X	XXX	X	XXX	XX	XXX	0	X	XXX
Crude Distillation	XXX	X	X	XX	XXX	XX	XXX	X	XX	XXX	X	0	X	X
Thermal Cracking	X	X	X	X	X	X		XX	XX	X	X	0	XX	X
Catalytic Cracking	XXX	XX	XX	XXX	XXX	X	X	XXX	XX	XXX	X	0	XXX	X
Hydrocracking	X			XX	XX				XX	XX				
Polymerization	X	X	X	0	X	X	0	X	X	X	X	X	0	X
Alkylation	XX	X	X	0	XX	X	0	XX	X	X	XX	XX	0	XX
Isomerization	X													
Reforming	X	0	0	X	X	X	0	0	X	X	0	0	0	0
Solvent Refining	X		X	X	0		X	X	0			0	X	
Asphalt Blowing	XXX	XXX	XXX	X		XXX								
Dewaxing	X	XXX	XXX	X	0	X	0							
Hydrotreating	X	X	X		XX		0	XX		XX	0	0	X	0
Drying and Sweetening	XXX	XXX	X	XX	0	0	X	XX	0	X	0	X	X	XX

XXX - Major Contribution, XX - Moderate Contribution, X - Minor Contribution, 0 - No Problem , -- No Data

1. STORAGE AND TRANSPORTATION

A. CRUDE OIL AND PRODUCT STORAGE

Process Description

Crude oil, intermediate, and finished products are stored in tanks of varying size to provide adequate supplies of crude oils for primary fractionation runs of economical duration, to equalize process flows and provide feedstocks for intermediate processing units, and to store final products prior to shipment in adjustment to market demands. Generally, operating schedules permit sufficient detention time for settling of water and suspended solids.

Wastes

Waste waters associated with storage of crude oil and products are mainly in the form of free and emulsified oil and suspended solids. During storage, water and suspended solids in the crude oil separate. The water layer accumulates below the oil, forming a bottom sludge. When the water layer is drawn off, emulsified oil present at the oil-water interface is often lost to the sewers. This waste is high in COD and contains a lesser amount of BOD5. Bottom sludge is removed at infrequent intervals. Additional quantities of waste result from leaks, spills, salt "filters" (for product drying), and tank cleaning.

Intermediate storage is frequently the source of polysulfide bearing waste waters and iron sulfide suspended solids. Finished product storage can produce high BOD5, alkaline waste waters, as well as tetraethyl lead. Tank cleaning can contribute large amounts of oil, COD, and suspended solids, and a minor amount of BOD5. Leaks, spills and open or poorly ventilated tanks can also be a source of air pollution, through evaporation of hydrocarbons into the atmosphere.

Trends

Many refineries now have storage tanks equipped to minimize the release of hydrocarbons to the atmosphere. This trend is expected to continue and probably accelerate. Equipment to minimize the release of hydrocarbon vapors includes tanks with floating-roof covers, pressurized tanks, and/or connections to vapor recovery systems. Floating-roof covers add to the waste water flow from storage tanks. Modern refineries impose strict Bottom Sediment and Water (BS&W) specifications on crude oil supplies, and frequently have mixed-crude storage tanks; consequently, little or no waste water should originate from modern crude storage. Another significant trend is toward increased use of dehydration or drying processes preceding product finishing. These processes significantly reduce the water content of finished product, thereby minimizing the quantity of waste water from finished product storage.

B. BALLAST WATER

Process Description

Tankers which are used to ship intermediate and final products generally arrive at the refinery in ballast (approximately 30 percent of the cargo capacity is generally required to maintain vessel stability).

Wastes

The ballast waters discharged by product tankers are contaminated with product materials which are the crude feedstock in use at the refinery, ranging from water soluble alcohol to residual fuels. In addition to the oil products contamination, brackish water and sediments are present, contributing high COD, and dissolved solids to the refinery waste water. These waste waters are generally discharged to either a ballast water tank or holding ponds at the refinery. In many cases, the ballast water is discharged directly to the waste water treatment system, and constitutes a shock load on the system.

Trends

As the size of tankers and refineries increases, the amount of ballast waters discharged to the refinery waste water system will also increase. The discharge of ballast water to the sea or estuary without treatment, as had been the previous practice by many tankers, is no longer a practical alternative for disposal of ballast water. Consequently, the ballast water will require treatment for the removal of pollutants prior to discharge. The use of larger ballast water storage tanks or ponds, for control of flow into the waste water treatment system, should increase as ballast water flow increases.

2. CRUDE DESALTING

Process Description

Common to all types of desalting are an emulsifier and settling tank. Salts can be separated from oil by either of two methods. In the first method, water wash desalting in the presence of chemicals (specific to the type of salts present and the nature of the crude oil) is followed by heating and gravity separation. In the second method, water wash desalting is followed by water/oil separation under the influence of a high voltage electrostatic field acting to agglomerate dispersed droplets. In either case, waste water containing various removed impurities is discharged to the waste stream, while clean desalted crude oil flows from the upper portion of the holding tank. A process flow schematic of electrostatic desalting is shown in Figure 1.

Wastes

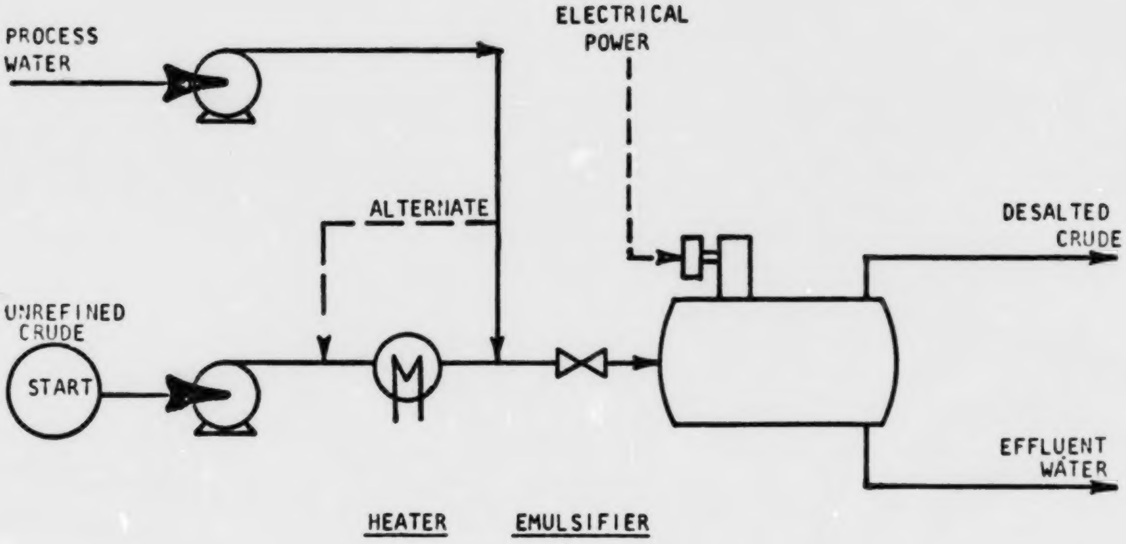


Figure 1

Crude Desalting
(Electrostatic Desalting)

Much of the BS&W content in crude oil is caused by the "Load-on-Top" procedure used on many tankers. This procedure can result in one or more cargo tanks containing mixtures of sea waters and crude oil, which cannot be separated by decantation while at sea, and are consequently retained in the crude oil storage at the refinery. While much of the water and sediment are removed from the crude oil by settling during storage, a significant quantity remains to be removed by desalting prior to processing of the crude in the refinery.

The continuous waste water stream from a desalter contains emulsified, and occasionally free oil, ammonia, phenol, sulfides, and suspended solids. These pollutants produce a relatively high BOD_5 and COD. This waste water also contains enough chlorides and other dissolved materials to contribute to the dissolved solids problem in the areas where the waste water is discharged to fresh water bodies. There are also potential thermal pollution problems because the temperature of the desalting waste water often exceeds 95°C (200°F).

Trends

Electrical desalting is currently used much more than chemical desalting. In the future, chemical methods are expected to be used only as a supplement where the crude has a very high salt content. Two stage electrical desalting will become a more prevelant process, as dirtier crude feedstocks are processed in refineries. The growth in capacity of desalting units will parallel the growth of crude oil capacity.

3. CRUDE OIL FRACTIONATION

Fractionation serves as the basic refining process for the separation of crude petroleum into intermediate fractions of specified boiling point ranges. The several alternative subprocesses included are prefractionation and atmospheric fractionation, vacuum fractionation, vacuum flashing, and three-stage crude distillation.

Process Description

Prefractionation and Atmospheric Distillation (Topping or Skimming)

Prefractionation is an optional distillation process to separate economical quantities of very light distillates from the crude oil. Lower temperature and higher pressure conditions are used than would be required in atmospheric distillation. Some process water can be carried over to the prefractionation tower from the desalting process.

Atmospheric Distillation breaks the heated crude oil as follows:

1. Light overhead products (C5 and lighter) as in the case of prefractionation.

2. Sidestream distillate cuts of kerosene, heating and gas oil can be separated in a single tower or in a series of topping towers, each tower yielding a successively heavier product stream.

3. Residual or reduced crude oil.

Vacuum Fractionation

The asphaltic residuum from the atmospheric distillation amounts to 37 percent (U.S. average) of the crude charged. This material is sent to vacuum stills, which recover additional heavy gas oil and deasphalting feedstock from the bottoms residue.

Three Stage Crude Distillation

Three stage crude distillation, representing only one of many possible combinations of equipment, is shown schematically in Figure 2. The process consists of:

1. An atmospheric fractioning stage which produces lighter oils;

2. An initial vacuum stage which produces well-fractioned, lube oil base stocks plus residue for subsequent propane deasphalting;

3. A second vacuum stage which fractionates surplus atmospheric bottoms not applicable for lube production, plus surplus initial vacuum stage residuum not required for deasphalting. This stage adds the capability of removing catalytic cracking stock from surplus bottoms to the distillation unit.

Crude oil is first heated in a simple heat exchanger, then in a direct-fired crude charge heater. Combined liquid and vapor effluent flow from the heater to the atmospheric fractionating tower, where the vaporized distillate is fractionated into gasoline overhead product and as many as four liquid sidestreams products:naphtha, kerosene, light and heavy diesel oil. Part of the reduced crude from the bottom of the atmospheric tower is pumped through a direct-fired heater to the vacuum lube fractionator. Bottoms are combined and charged to a third direct-fired heater. In the tower, the distillate is subsequently condensed and withdrawn as two sidestreams. The two sidestreams are combined to form catalytic cracking feedstocks, with an asphalt base stock withdrawn from the tower bottom.

Wastes

The waste water from crude oil fractionation generally comes from three sources. The first source is the water drawn off from overhead accumulators prior to recirculation or transfer of hydrocarbons to other fractionators. This waste is a major source of sulfides and ammonia, especially when sour crudes are

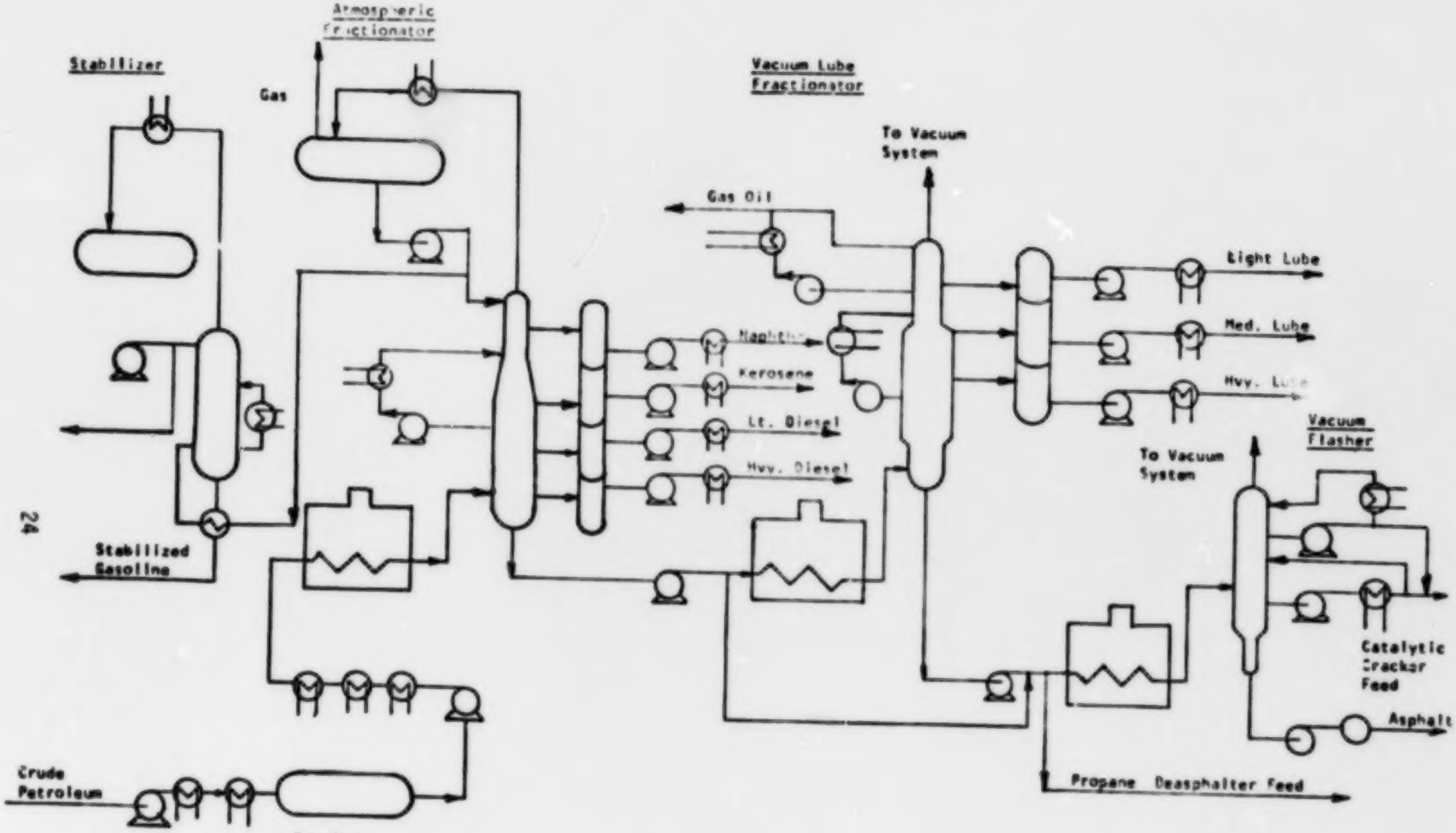


Figure 2

CRUDE FRACTIONATION
(CRUDE DISTILLATION, THREE STAGES)

being processed. It also contains significant amounts of oil, chlorides, mercaptans and phenols.

A second waste source is discharged from oil sampling lines. This should be separable but may form emulsions in the sewer.

A third possible waste source is the very stable oil emulsions formed in the barometric condensers used to create the reduced pressures in the vacuum distillation units. However, when barometric condensers are replaced with surface condensers, oil vapors do not come in contact with water; consequently, emulsions do not develop.

Trends

The general industry trend to larger and more complete refineries has been reflected also in larger and more complete crude fractionation units. Thus, simple atmospheric "topping" units are being replaced by the atmospheric- vacuum combinations with an increasing number of sidestream products. Installed vacuum fractionation capacity now totals, 0.8 million cu m/day (5 million bbl/day). (3) Modern refineries are installing surface condensers to significantly reduce waste water loads from vacuum operations.

4. CRACKING

A. THERMAL CRACKING

Process Description

This fundamental process is defined in this study to include visbreaking and coking, as well as regular thermal cracking. In each of these operations, heavy gas oil fractions (from vacuum stills) are broken down into lower molecular weight fractions such as domestic heating oils, catalytic cracking stock, and other fractions by heating, but without the use of a catalyst. Typical thermal cracking conditions are 480° - 603°C, (900° - 1100°F) and 41.6 - 69.1 atm (600-1000 psig). The high pressures result from the formation of light hydrocarbons in the cracking reaction (olefins, or unsaturated compounds, are always formed in this chemical conversion). There is also always a certain amount of heavy fuel oil and coke formed by polymerization and condensation reactions.

Wastes

The major source of waste water in thermal cracking is the overhead accumulator on the fractionator, where water is separated from the hydrocarbon vapor and sent to the sewer system. This water usually contains various oil and fractions and may be high in BOD5, COD, ammonia, phenol, and sulfides, and may have a high alkalinity.

Trends

Regular thermal cracking, which was an important process before the development of catalytic cracking, is being phased out. Visbreaking and coking units are still installed but, because of product sulfur restrictions, to a lesser extent than before. With the trends toward dirtier crudes containing more sulfur, hydrocracking and propane deasphalting are receiving more attention to recover salable products with low sulfur content from the residuum.

B. CATALYTIC CRACKING

Process Description

Catalytic cracking, like thermal cracking, breaks heavy fractions, principally gas oils, into lower molecular weight fractions. This is probably the key process in the production of large volumes of high-octane gasoline stocks; furnace oils and other useful middle molecular weight distillates are also produced. The use of a catalyst permits operations at lower temperatures and pressures than with thermal cracking, and inhibits the formation of undesirable polymerized products. Fluidized catalytic processes, in which the finely powdered catalyst is handled as a fluid, have largely replaced the fixed bed and moving bed processes, which use a beaded or pelleted catalyst. A schematic flow diagram of fluid catalytic cracking is shown in Figure 3.

The process involves at least four types of reactions: 1) thermal decomposition; 2) primary catalytic reactions at the catalyst surface; 3) secondary catalytic reactions between the primary products, and 4) removal of polymerizable products from further reactions by absorption onto the surface of the catalyst as coke. This last reaction is the key to catalytic cracking because it permits decomposition reactions to move closer to completion than is possible in simple thermal cracking. Cracking catalysts include synthetic and/or natural silica-alumina, treated bentonite clay, Fuller's earth, aluminum hydrosilicates and bauxite. These catalysts are in the form of beads, pellets, and powder, and are used in either a fixed, moving or fluidized bed. The catalyst is usually heated, lifted into the reactor area by the incoming oil feed which, in turn, is immediately vaporized upon contact. Vapors from the reactors pass upward through a cyclone separator, which removes most of the entrained catalyst. These vapors then enter the fractionator, where the desired products are removed and heavier fractions recycled to the reactor.

Wastes

Catalytic cracking units are one of the largest sources of sour and phenolic wastewaters in a refinery. Pollutants from catalytic cracking generally come from the steam strippers and overhead accumulators on fractionators, used to recover and separate the various hydrocarbon fractions produced in the catalytic reactors.

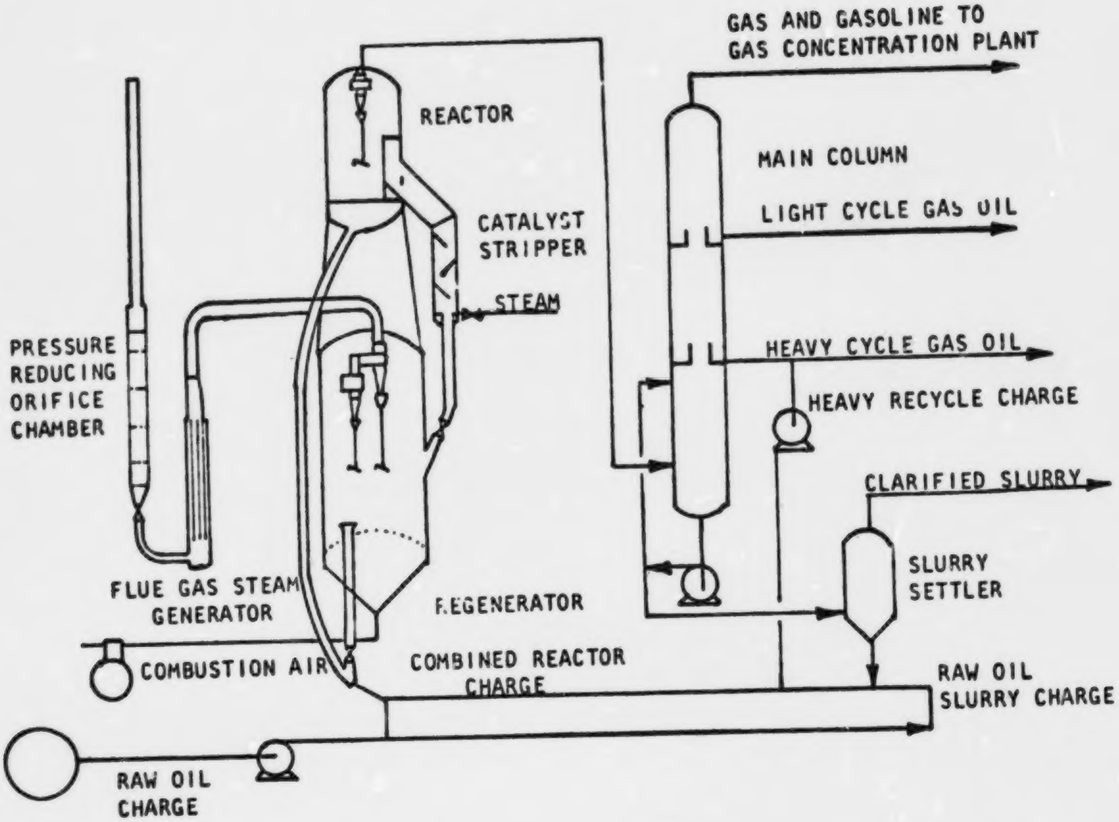


Figure 3

CATALYTIC CRACKING

(FLUID CATALYTIC CRACKING)

The major pollutants resulting from catalytic cracking operations are oil, sulfides, phenols, cyanides, and ammonia. These pollutants produce an alkaline waste water with high BOD_5 and COD concentrations. Sulfide and phenol concentrations in the waste water vary with the type of crude oil being processed, but at times are significant. Regeneration of spent catalyst may produce enough carbon monoxide and catalyst fines to constitute an air pollution problem.

Trends

Recycle rates have been declining since 1968, and the trend is expected to continue due to the development of higher activity catalysts (molecular sieve catalysts, as opposed to high surface area silica-alumina catalysts). The trend in subprocesses is toward greater use of large fluid catalytic cracking in preference to moving or fixed-bed cracking. Catalytic cracking units are also being supplanted by hydrocracking and hydrotreating processes. During 1972, a decline of 1.4 percent in fresh feed catalytic cracking capacity was experienced in the United States. (3)

C. HYDROCRACKING

Process Description

This process is basically catalytic cracking in the presence of hydrogen, with lower temperatures and higher pressures than fluid catalytic cracking. Hydrocracking temperatures range from 203° - 425°C (400° - 800°F), while pressures range from 7.8 - 137.0 atm (100 to 2000 psig). Actual conditions and hydrogen consumption depend upon the feedstock, and the degree of hydrogenation required. The molecular weight distribution of the products is similar to catalytic cracking, but with the reduced formation of olefins.

Wastes

At least one waste water stream from the process should be high in sulfides, since hydrocracking reduces the sulfur content of the material being cracked. Most of the sulfides are in the gas products which are sent to a treating unit for removal and/or recovery of sulfur and ammonia. However, in product separation and fractionation units following the hydrocracking reactor, some of the HS will dissolve in the waste water being collected. This water from the separator and fractionator will probably be high in sulfides, and possibly contain significant quantities of phenols and ammonia.

Trends

Hydrocracking has greater flexibility than catalytic cracking in adjusting operations to meet changing product demands. For the last few years, it has been one of the most rapidly growing refining processes. This trend is expected to continue.

5. HYDROCARBON REBUILDING

A. POLYMERIZATION

Process Description

Polymerization units are used to convert olefin feedstocks (primarily propylene) into higher octane polymer units. These units generally consist of a feed treatment unit (remove H_2S, mercaptans, nitrogen compounds), a catalytic reactor, an acid removal section, and a gas stabilizer. The catalyst is usually phosphoric acid, although sulfuric acid is used in some older methods. The catalytic reaction occurs at 147° - 224°C (300° - 435°F), and a pressure of 11.2 - 137.0 atm (150 - 2000 psig). The temperature and pressure vary with the individual subprocess used.

Wastes

Polymerization is a rather dirty process in terms of pounds of pollutants per barrel of charge, but because of the small polymerization capacity in most refineries, the total waste production from the process is small. Even though the process makes use of acid catalysts, the waste stream is alkaline, because the acid catalyst in most subprocesses is recycled, and any remaining acid is removed by caustic washing. Most of the waste material comes from the pretreatment of feedstock to the reactor. The waste water is high in sulfides, mercaptans, and ammonia. These materials are removed from the feedstock in caustic acid.

Trends

Polymerization is a marginal process, since the product octane is not significantly higher than that of the basic gasoline blending stocks, and does not provide much help in upgrading the overall motor fuel pool. In addition, alkylation yields per unit of olefin feed are much better than polymerization yields. Consequently, the current polymerization downtrend is expected to continue.

B. ALKYLATION

Process Description

Alkylation is the reaction of an isoparaffin (usually isobutane) and an olefin (propylene, butylene, amylenes) in the presence of a catalyst at carefully controlled temperatures and pressures to produce a high octane alkylate for use as a gasoline blending component. Propane and butane are also produced. Sulfuric acid is the most widely used catalyst, although hydrofluoric acid is also used. The reactor products are separated in a catalyst recovery unit, from which the catalyst is recycled. The hydrocarbon stream is passed through a caustic and water wash before going to the fractionation section.

Wastes

The major discharge from sulfuric acid alkylation are the spent caustics from the neutralization of hydrocarbon streams leaving the sulfuric acid alkylation reactor. These waste waters contain dissolved and suspended solids, sulfides, oils, and other contaminants. Water drawn off from the overhead accumulators contains varying amounts of oil, sulfides, and other contaminants, but is not a major source of waste in this subprocess. Most refineries process the waste sulfuric acid stream from the reactor to recover clean acids, use it as if for neutralization of other waste streams, or sell it.

Hydrofluoric acid alkylation units have small acid rerun units to purify the acid for reuse. HF units do not have a spent acid or spent caustic waste stream. Any leaks or spills that involve loss of fluorides constitute a serious and difficult pollution problem. Formation of fluosilicates has caused line plugging and similar problems. The major sources of waste material are the overhead accumulators on the fractionator.

Trends

Alkylation process capacity is currently declining slowly, but this trend may be reversed, as the demand for low lead, high octane gasoline increases.

6. HYDROCARBON REARRANGEMENTS

A. ISOMERIZATION

Process Description

Isomerization is a process technique for obtaining higher octane motor fuel by converting light gasoline stocks into their higher octane isomers. The greatest application has been, indirectly, in the conversion of isobutane from normal butane, for uses as feedstock for the alkylation process. In a typical subprocess, the desulfurized feedstock is first fractionated to separate isoparaffins from normal paraffins. The normal paraffins are then heated, compressed, and passed through the catalytic hydrogenation reactor which isomerizes the n-paraffin to its respective high octane isomer. After separation of hydrogen, the liquids are sent to a stabilizer, where motor fuel blending stock or synthetic isomers are removed as products.

Wastes

Isomerization waste waters presert no major pollutant discharge problems. Sulfides and ammonia are not likely to be present in the effluent. Isomerization waste waters should also be low in phenolics and oxygen demand.

Trends

The requirements for units to isomerize n-butane to isobutane will not be as great in refineries where hydrocracking is being installed, as the hydrocracking process yields an off-gas rich in isobutane. However, the isomerization capacity of U.S. refiners is not expected to decrease, but to continue to grow as the demand for motor fuel grows.

B. REFORMING

Process Description

Reforming converts low octane naphtha, heavy gasoline, and napthene-rich stocks, to high octane gasoline blending stock, aromatics for petro-chemical use, and isobutane. Hydrogen is a significant by-product of the process. Reforming is a mild decomposing process, since some reduction occurs in molecular size and boiling range of the feedstock. Feedstocks are usually hydrotreated for the removal of sulfur and nitrogen compounds prior to charging to the reformer, since the platinum catalysts widely used are readily poisoned.

The predominant reaction during reforming is the dehydrogenation of naphthenes. Important secondary reactions are the isomerization and dehydrocyclization of paraffins. All three reactions result in higher octane products.

One subprocess may be divided into three parts: the reactor heater section, in which the charge plus recycle gas is heated and passed over the catalyst in a series of reactions; the separator drum, in which the reactor effluent is separated into gas and liquid streams, the gas being compressed for recycle; and the stabilizer section, in which the separated liquid is stabilized to the desired vapor pressure. There are many variations in subprocesses, but the essential, and frequently the only, difference is the composition of the catalyst involved.

Wastes

Reforming is a relatively clean process. The volume of waste water flow is small, and none of the waste water streams has high concentration of significant pollutants. The waste water is alkaline, and the major pollutant is sulfide from the overhead accumulator on the stripping tower used to remove light hydrocarbon fractions from the reactor effluent. The overhead accumulator catches any water that may be contained in the hydrocarbon vapors. In addition to sulfides, the waste water contains small amounts of ammonia, mercaptans and oil.

Trends

Reforming capacity in the U.S. is currently growing at about the same rate as total crude capacity. This growth rate may increase, however, as the demand for motor fuel grows.

7. SOLVENT REFINING

Refineries employ a wide spectrum of contact solvent processes, which are dependent upon the differential solubilities of the desirable and undesirable feedstock components. The principal steps are: counter-current extraction, separation of solvent and product by heating and fractionation, and solvent recovery. Napthenics, aromatics unsaturated hydrocarbons, sulfur and other inorganics are separated, with the solvent extract yielding high purity products. Many of the solvent processes may produce process waste waters which contain small amounts of the solvents employed. However, these are ususally minimized, because of the economic incentives for reuse of the solvents.

Process Description

The major processes include:

Solvent Deasphalting - The primary purpose of solvent deasphalting is to recover lube or catalytic cracking feedstocks from asphaltic residuals, with asphalt as a by-product. Propane deasphalting is the predominant technique. The vacuum fractionation residual is mixed in a fixed proportion with a solvent in which asphalt is not soluble. The solvent is recovered from the oil via steam stripping and fractionation, and is reused. The asphalt produced by this method is normally blended into fuel oil or other asphaltic residuals.

Solvent Dewaxing - Solvent dewaxing removes wax from lubricating oil stocks by promoting crystallization of the wax. Solvents which are used include: furfural, phenol, cresylic acid - propane (Duo-Sol), liquid sulfur dioxide (Eleleanu process), B-B - dichloroethyl ether, methyl ethyl ketone, nitrobenzene, and sulfur-benzene. The process yields de-oiled waxes, wax-free lubricating oils, aromatics, and recovered solvents.

Lube Oil Solvent Refining - This process includes a collection of subprocesses for improving the quality of lubricating oil stock. The raffinate or refined lube oils obtain improved temperature, viscosity, color and oxidation resistance characteristics. A particular solvent is selected to obtain the desired quality raffinate. The solvents include: furfural, phenol, sulfur dioxide, and propane.

Aromatic Extraction - Benzene, toluene, and xylene (BTX) are formed as by-products in the reforming process. The reformed products are fractionated to give a BTX concentrate cut, which in turn is extracted from the napthalene and the paraffinics with a glycol base solvent.

Butadiene Extraction - Approximately 15 percent of the U.S. supply of butadiene is extracted from the C4 cuts from the high temperature petroleum cracking processes. Furfural or cuprous ammonia acetate (CAA) are commonly used for the solvent extraction.

Wastes

The major potential pollutants from the various solvent refining subprocesses are the solvents themselves. Many of the solvents, such as phenol, glycol, and amines, can produce a high BOD5. Under ideal conditions the solvents are continually recirculated with no losses to the sewer. Unfortunately, some solvent is always lost through pump seals, flange leaks, and other sources. The main source of waste water is from the bottom of fractionation towers. Oil and solvent are the major waste water constituents.

Trends

Solvent extraction capacities can be expected to slowly increase as quality requirements for all refinery products become more stringent, as the demand for lube oils grows, and as the petrochemicals industry continues to require increasing quantities of aromatics.

8. HYDROTREATING

Process Description

Hydrotreating processes are used to saturate olefins, and to remove sulfur and nitrogen compounds, odor, color and gum-forming materials, and others by catalytic action in the presence of hydrogen, from either straight-run or cracked petroleum fractions. In most subprocesses, the feedstock is mixed with hydrogen, heated, and charged to the catalytic reactor. The reactor products are cooled, and the hydrogen, impurities and high grade product separated. The principal difference between the many subprocesses is the catalyst; the process flow is similar for essentially all subprocesses.

Hydrotreating processes are used to reduce the sulfur content of product streams from sour crudes by approximately 90 percent or more. Nitrogen removal requires more severe operating conditions, but generally 80 - 90 percent, or better, reductions are accomplished.

The primary variables influencing hydrotreating are hydrogen partial pressure, process temperature, and contact time. An increase in hydrogen pressure gives a better removal of undesirable materials and a better rate of hydrogenation. Make-up hydrogen requirements are generally high enough to require a hydrogen production unit. Excessive temperatures increase the formation of coke, and the contact time is set to give adequate treatment without excessive hydrogen usage and/or undue coke formation. For the various hydrotreating processes the pressures range from 7.8 - 205.1 atm (100 to 3000 psig). Temperatures range from less than 177°C (350°F) to as high as 450°C (850°F), with most processing done in the range of 314°C (600°F) to 427°C (800°F). Hydrogen consumption is usually less than 5.67 NM^3 (200 scf) per barrel of charge.

Principal hydrotreating subprocesses are used as follows:

1. Pretreatment of catalytic reformer feedstock.
2. Naphtha desulfurization.
3. Lube oil polishing.
4. Pretreatment of catalytic cracking feedstock.
5. Heavy gas-oil and residual desulfurization.
6. Naphtha saturation.

Wastes

The strength and quantity of waste waters generated by hydrotreating depends upon the subprocess used and feedstock. Ammonia and sulfides are the primary contaminants, but phenols may also be present, if the feedstock boiling range is sufficiently high.

Trends

The use of hydrotreating is increasing and should continue to increase at a greater rate than crude capacity since the process can be applied to almost any sour feedstock, is flexible, and eliminates contaminants of concern to the refining industry from an operating standpoint, and to the general public from an aesthetic standpoint.

9. GREASE MANUFACTURING

Process Description

Grease manufacturing processes require accurate weight or volumetric measurements of feed components, intimate mixing, rapid heating and cooling, together with milling, dehydration and polishing in batch reactions. The feed components include soap and petroleum oils, with inorganic clays and other additives.

Grease is primarily a soap and lube oil mixture. The properties of grease are determined in large part by the properties of the soap component. For example, sodium metal base soaps are water soluble and would then not be suitable for water contact service. A calcium soap grease can be used in water service. The soap may be purchased as a raw material or may be manufactured on site as an auxiliary process.

Wastes

Only very small volumes of waste water are discharged from a grease manufacturing process. A small amount of oil is lost to the waste water system through leaks in pumps. The largest waste loading occurs when the batch units are washed, resulting in soap and oil discharges to the sewer system.

Trends

Because of an increase in sealed grease fittings in automobiles and longer lasting greases, a slight decline in grease production is expected through 1975.

10. ASPHALT PRODUCTION

Process Description

Asphaltic feedstock (flux) is contacted with hot air at 203°C (400°F) to 280°C (550°F) to obtain desirable asphalt product. Both batch and continuous processes are in operation at present, but the batch process is more prevalent because of its versatility. Nonrecoverable catalytic compounds include: Copper sulfate, zinc chloride, ferric chloride, aluminum chloride, phosphorous pentoxide, and others. The catalyst will not normally contaminate the process water effluent.

Wastes

Waste waters from asphalt blowing contain high concentrations of oils, and have high oxygen demand. Small quantities of phenols may also be present.

11. PRODUCT FINISHING

A. DRYING AND SWEETENING

Process Description

Drying and sweetening is a relatively broad process category primarily used to remove sulfur compounds, water and other impurities from gasoline, kerosene, jet fuels, domestic heating oils, and other middle distillate products. "Sweetening" pertains to the removal of hydrogen sulfide, mercaptans and thiophenes, which impart a foul odor and decrease the tetra-ethyl lead susceptibility of gasoline. The major sweetening operations are oxidation of mercaptans or disulfides, removal of mercaptans, and destruction and removal of all sulfur compounds. Drying is accomplished by salt filters or absorptive clay beds. Electric fields are sometimes used to facilitate separation of the product.

Wastes

The most common waste stream from drying and sweetening operations is spent caustic. The spent caustic is characterized as phenolic or sulfidic, depending on which is present in the largest concentration. Whether the spent caustic is actually phenolic or sulfidic is mainly determined by the product stream being treated. Phenolic spent caustics contain phenol, cresols, xylenols, sulfur compounds, and some neutral oils. Sulfidic spent caustics are rich in sulfides, but do not contain any phenols. These spent caustics have very high BOD_5 and COD. The phenolic caustic streams are usually sold for the recovery of phenolic materials.

Other waste streams from the process result from water washing of the treated product and regeneration of the treating solution such as sodium plumbite ($No_2 PbO_2$) in doctor sweetening. These waste streams will contain small amounts of oil and the treating material, such as sodium plumbite (or copper from copper chloride sweetening).

The treating of sour gases produces a purified gas stream, and an acid gas stream rich in hydrogen sulfide. The H2S rich stream can be flared, burned as fuel, or processed for recovery of elemental sulfur.

Trends

As air pollution agencies increase their efforts to control sulfur emissions to the atmosphere, the restrictions on sulfur content in fuels can be expected to tighten. This will generate a strong trend to replacement of the sweetening processes by more hydrotreating (desulfurization), because hydrotreating removes almost all sulfur compounds and not just hydrogen sulfide, mercaptans, and elemental sulfur. Nevertheless, on certain feedstocks sweetening will continue to be used because it will be as effective as, and more economical than, hydrotreating. Those processes producing high waste loads (Doctor Sweetening, etc.) are being replaced by lower waste-producing processes.

B. LUBE OIL FINISHING

Process Description

Solvent refined and dewaxed lube oil stocks can be further refined by clay or acid treatment to remove color-forming and other undesirable materials. Continuous contact filtration, in which an oil-clay slurry is heated and the oil removed by vacuum filtration, is the most widely used subprocess.

Wastes

Acid treatment of lubricating oils produces acid bearing wastes occuring as rinse waters, sludges, and discharges from sampling, leaks and shutdowns. The waste streams are also high in dissolved and suspended solids, sulfates, sulfonates, and stable oil emulsions.

Handling of acid sludge can create additional problems. Some refineries burn the acid sludge as fuel. Burning the sludge produces large volumes of sulfur dioxide that can cause air pollution problems. Other refineries neutralize the sludge with alkaline wastes and discharge it to the sewer, resulting in both organic and inorganic pollution. The best method of disposal is probably processing to recover the sulfuric acid, but this also produces a waste water stream containing acid, sulfur compounds and emulsified oil.

Clay treatment results in only small quantities of waste water being discharged to the sewer. Clay, free oil, and emulsified oil are the major waste constituents. However, the operation of clay recovery kilns involves potential air pollution problems of hydrocarbon and particulate emissions. Spent clays usually are disposed of by landfill.

Trends

Acid and clay treatment of lube oils is gradually being replaced by hydrotreating methods. Acid treatment in particular is being phased out rather rapidly.

C. BLENDING AND PACKAGING

Process Description

Blending is the final step in producing finished petroleum products to meet quality specifications and market demands. The largest volume operation is the blending of various gasoline stocks (including alkylates and other high-octane components) and anti-knock (tetra-ethyl lead), anti-rust, anti-icing, and other additives. Diesel fuels, lube oils, and waxes involve blending of various components and/or additives. Packaging at refineries is generally highly-automated and restricted to high volume, consumer-oriented products such as motor oils.

Wastes

These are relatively clean processes because care is taken to avoid loss of product through spillage. The primary source of waste material is from the washing of railroad tank cars or tankers prior to loading finished products. These wash waters are high in emulsified oil.

Tetra-ethyl lead is the major additive blended into gasoline and it must be carefully handled because of its high toxicity. Sludges from finished gasoline storage tanks can contain large amounts of lead and should not be washed into the wastewater system.

Trends

There will be an increased use of automatic proportioning facilities for product blending with a trend toward contracting out of packaging of lower-volume products that are less suitable to highly-automated operation.

12. AUXILIARY ACTIVITIES

A. HYDROGEN MANUFACTURE

Process Description

The rapid growth of hydrotreating and hydrocracking has increased the demand for hydrogen beyond the level of by-product hydrogen available from reforming and other refinery processes. The most widely used process for the manufacture of hydrogen in the refinery is steam reforming, which utilizes refinery gases as a charge stock. The charge is purified to remove sulfur compounds that would temporarily deactivate the catalysts.

The desulfurized feedstock is mixed with superheated steam and charged to the hydrogen furnace. On the catalyst the hydrocarbons are converted to hydrogen, carbon monoxide, and carbon dioxide. The furnace supplies the heat needed to maintain the reaction temperature.

The gases from the furnace are cooled by the addition of condensate and steam, and then passed through a converter containing a high- or low-temperature shift catalyst depending on the degree of carbon monoxide conversion desired. Carbon dioxide and hydrogen are produced by the reaction of the monoxide with steam.

The gas mixture from the converter is cooled and passes to a hydrogen purifying system where carbon dioxide is absorbed into amine solutions and later driven off to the atmosphere by heating the rich amine solution into the reactivator.

Since some refining processes require a minimum of carbon oxides in the product gas, the oxides are reacted with hydrogen in a methanation step. This reaction takes place in the methanator over a nickel catalyst at elevated temperatures.

Hydrocarbon impurities in the product hydrogen usually are not detrimental to the processes where this hydrogen will be used. Thus, a small amount of hydrocarbon is tolerable in the effluent gas.

Wastes

Information concerning wastes from this process are not available. However, the process appears to be a relatively clean one. In the steam reforming subprocess a potential waste source is the desulfurization unit, which is required for feedstock that has not already been desulfurized. This waste stream would contain oil, sulfur compounds, and phenol. In the partial oxidation subprocess free carbon is removed by a water wash. Carbon dioxide is discharged to the atmosphere at several points in the subprocess.

Trends

Hydrogen requirements of the rapidly growing hydrocracking and hydrotreating processes in many instances exceed the by-product hydrogen available from catalytic reforming units. Since hydrocracking and hydrotreating are expected to grow more rapidly than other refinery processes, the demand for hydrogen manufacturing units should continue to be strong.

B. UTILITIES FUNCTION

Utility functions such as the supply of steam and cooling water generally are set up to service several processes. Boiler feed water is prepared and steam is generated in a single boiler house. Non-contact steam used for surface heating is circulated through a closed loop whereby varying quantities are made available for the specific requirements of the different processes. The condensate is nearly always recycled to the boiler house, where a certain portion is discharged as blowdown.

The three major uses of steam generated within a refinery plant are:

1. For non-contact process heating. In this application, the steam is normally generated at pressures of 9.5 to 45.2 atm (125 to 650 psig).
2. For power generation such as in steam-driven turbines, compressors, and pumps associated with the process. In this application, the steam is normally generated at pressures of 45.2 to 103 atm (650 to 1500 psig) and requires superheating.
3. For use as a diluent, stripping medium, or source of vacuum through the use of steam jet ejectors. This steam actually contacts the hydrocarbons in the manufacturing processes and is a source of contact process waste water when condensed. It is used at a substantially lower pressure than the foregoing and frequently is exhaust steam from one of the other uses.

Steam is supplied to the different users throughout the plant either by natural- circulation, vapor-phase systems, or by forced-circulation liquid heat-transfer systems. Both types of systems discharge some condensate as blowdown and require the addition of boiler make-up water. The main areas of consideration in boiler operation are normally boiler efficiency, internal deposits, corrosion, and the required steam quality.

Boiler efficiency is dependent on many factors. One is the elimination of boiler-tube deposition that impedes heat transfer. The main contributors to boiler deposits are calcium, magnesium, silicon, iron, copper, and aluminum. Any of these can occur in natural waters, and some can result from condensate return-line corrosion or even from make-up water pretreatment. Modern industrial boilers are designed with efficiencies on the order of 80 percent. A deposit of 0.32 cm (1/8 inch) in depth will cause a 2-3 percent drop in this efficiency, depending on the type of deposit.

Internal boiler water treatment methods have advanced to such a stage that corrosion in the steam generation equipment can be virtually eliminated. The control of caustic embrittlement in boiler tubes and drums is accomplished through the addition of sodium nitrate in the correct ratio to boiler water alkalinity.

Caustic corrosion in high heat transfer boilers can also be controlled by the addition of chelating agents. This type of solubilizing internal boiler water treatment has been shown to be more effective than previous precipitation treatment using phosphate.

Other factors influencing boiler efficiency include reduction of the amount of boiler blowdown by increasing cycles of concentration of the boiler feedwater, efficiency of the blowdown heat-recovery equipment, and the type of feed used.

Steam purity is of prime importance if:

1. The boilers are equipped with superheaters.
2. The boilers supply power-generation equipment.
3. The steam is used directly in a process where contamination could affect product quality or destroy some material (such as a catalyst) essential to the manufacture of the product.

The minimum purity required for contact steam (or contact process water) varies from process to process. Limits for suspended solids, total solids, and alkalinity vary inversely with the steam pressure. The following tabulation summarizes boiler water concentration limits for a system providing a steam purity of 0.5 - 1.0 ppm total solids, which is required for most non-contact steam uses. It should be noted that the boiler operation must incorporate the use of antifoam agents and steam separation equipment for the concentrations shown to be valid.

Boiler Water Concentration Required to
Maintain Steam Purity at 0.5 - 1.0 ppm Total Solids

	Boiler Pressure, atm.			
Parameters	21.4	21.5 - 31.6	31.7 -41.8	41.9 - 52.0
Total Solids (mg/l)	6,000	5,000	4,000	2,500
Suspended Solids(mg/l)	1,000	200	100	50
Total Alkalinity(mg/l)	1,000	900	800	750

Water conditioning or pretreatment systems are normally part of the utilities section of most plants. From the previous discussions, it is obvious that the required treatment may be quite extensive. Ion-exchange demineralization systems are very widely employed, not only for conditioning water for high-pressure boilers, but also for conditioning various process waters. Clarification is also widely practiced and usually precedes the ion-exchange operation.

Non-contact cooling water also is normally supplied to several processes from the utilities area. The system is either a loop which utilizes one or more evaporative cooling towers, or a once-through system with direct discharge.

Cooling towers accomplish the cooling of water circulated over the tower by moving a predetermined flow of ambient air through the tower with large fans. The air water contact causes a small amount of the water to be evaporated by the air. Thus, through latent heat transfer, the remainder of the circulated water is cooled.

Approximately 252 kg cal (1,000 BTU) are removed from the total water circulation by the evaporation of 0.454 kg (1 lb) of water. Therefore, if 45.4 kg (100 lbs) of water are introduced at the tower inlet and 0.454 kg (1 lb) is evaporated to the moving air, the remaining 44.9 kg (99 lbs) of water are reduced in total heat content by 252 kg cal (1,000 BTU), of water leaving the tower have been cooled 3.24°C/kg/kg cal (1°F/lb/BTU removed, and the exit temperature is reduced by about 5,500 (10°F). This leads to the common rule of thumb: 1 percent evaporation loss for each 5.5°C (10°F) cooling.

Since cooling is primarily by transfer of latent heat, cooling tower selection is based on the total heat content or enthalpy of the entering air. At any one enthalpy condition, the wet bulb temperature is constant. Therefore, cooling towers are selected and guaranteed to cool a specific volume of water from a hot-water temperature to a cold-water temperature while operating at a design wet-bulb temperature. Design wet-bulb temperatures vary from 15.6°C (60°F) to 35°C (85°F) depending on the geographic area, and are usually equaled or exceeded only 2.5 percent to 5 percent of the total summer operating time.

Hot water temperature minus cold water temperature is termed cooling range, and the difference between cold water and wet-bulb temperature is called approach.

A closed system is normally used when converting from once-through river cooling of plant processes. In the closed system, a cooling tower is used for cooling all of the hot water from the processes. With the closed system, make-up water from the river is required to replace evaporation loss at the tower.

Two other water losses also occur. The first is drift, which is droplet carryover in the air as contrasted to evaporative loss. The cooling tower industry has a standarized guarantee that drift loss will not exceed 0.2 percent of the water circulated. The second loss in the closed system is blowdown to sewer or river. Although blowdown is usually taken off the hot water line, it may be removed from the cold water stream in order to comply with regulations that limit the temperature of water returned to the stream. Blowdown from a tower system will vary depending on the solids concentration in the make-up water, and on the occurrence of solids that may be harmful to equipment. Generally, blowdown will be about 0.3 percent per 5.5°C (10°F) of cooling, in order to maintain a solids concentration in the recirculated water of three to four times that of the make-up water.

The quantity and quality of the blowdown form boilers and cooling towers depend on the design of the particular plant utility system. The heat content of these streams is purely a function of the heat recovery equipment associated with the utility system. The amounts of waste brine and sludge produced by ion exchange and water treatment systems depend on both the plant water use function and the intake source. None of these utility waste streams can be related directly to specific process units.

Quantitative limitations on parameters such as dissolved solids, hardness, alkalinity, and temperature, therefore, cannot be allocated on a production basis. The limitations on such parameters associated with non-contact utility effluents should be established on the basis of the water quality criteria of the specific receiving water body or an EPA study of all industries, to define specific utility effluent limitations.

Refinery Distribution

There are a total of 252 operating petroleum refineries in the United States, Puerto Rico and the Virgin Islands, as of January 1, 1973, with a combined capacity of 2.24 million cu m/day (14 million barrels/day) of crude oil processing (see Figure 4 and Table 10). The capacity of these plants range from 32 cu m/day (200 bbl/day) to 69,000 cu m/day (434,000 bbl/day) of crude oil.

Within the United States, refineries are concentrated in areas of major crude production (California, Texas, Louisiana, Oklahoma, Kansas), and in major population areas (Illinois, Indiana, Ohio, Pennsylvania, Texas, and California).

There are an almost unlimited number of process combinations possible within the process area, or "Battery Limits", of the typical refinery. Selection of the processing route for the manufacture of a particular product mix at a particular location or time is a decision based on the particular refiner's unique situation. In order to illustrate the diversity of operations which may be included within a refinery, Figure 5 shows the schematic flow diagram for a hypothetical 15,900 cu m/day (100,000 bbl/day) integrated refinery. This hypothetical refinery includes essentially all production processes previously outlined; hence the hypothetical refinery shown in Figure 5 is completely integrated for current U.S. refinery capacity. Inspection of Table 11 demonstrates the general distribution of refining processes.

The trend in the petroleum refining industry is toward fewer and larger refineries, which are integrated with satellite or companion industries. This consolidation trend for a six-year period (1967-1973) is shown in Table 12. Refineries with capacities over 15,900 cu m/day (100,000 bbl/day) (11.5 percent of the total) represented 48 percent of the domestic refinery

TABLE 10

CRUDE CAPACITY OF PETROLEUM REFINERIES BY STATES AS OF JANUARY 1, 1974 (3)

State	Number of Plants	Cubic Meters/Day	Rated Crude Capacity Barrels/Day
Alabama	4	5,885	37,010
Alaska	4	10,970	69,020
Arizona	1	1,590	10,000
Arkansas	4	9,220	58,000
California	34	301,270	1,894,800
Colorado	3	9,210	57,920
Delaware	1	23,850	150,000
Florida	1	875	5,500
Georgia	2	2,410	15,130
Hawaii	2	11,720	73,689
Illinois	11	191,820	1,206,390
Indiana	7	93,500	588,050
Kansas	11	66,470	418,050
Kentucky	3	26,550	167,000
Louisiana	18	275,580	1,733,180
Maryland	2	3,930	24,740
Michigan	6	23,410	147,230
Minnesota	3	31,480	198,000
Mississippi	5	47,440	298,390
Missouri	1	17,570	110,530
Montana	8	26,430	166,200
Nebraska	1	875	5,500
New Jersey	5	102,735	646,131
New Mexico	6	9.080	57,130
New York	2	17,650	111,000
North Dakota	2	8,790	55,300
Ohio	7	96,430	606,500
Oklahoma	12	79,130	497,695
Oregon	1	2,340	14,740
Pennsylvania	11	115,945	729,215
Tennessee	1	4,770	30,000
Texas	40	619,550	3,896,560
Utah	6	22,360	140,620
Virginia	1	8,870	55,790
Washington	7	57,400	361,100
West Virginia	3	3,260	20,500
Wisconsin	1	6,040	38,000
Wyoming	10	28,810	181,210
Puerto Rico	3	46,269	291,000
Virgin Islands	1	71,550	450,000
TOTAL	251	2,483,110	15,617,050

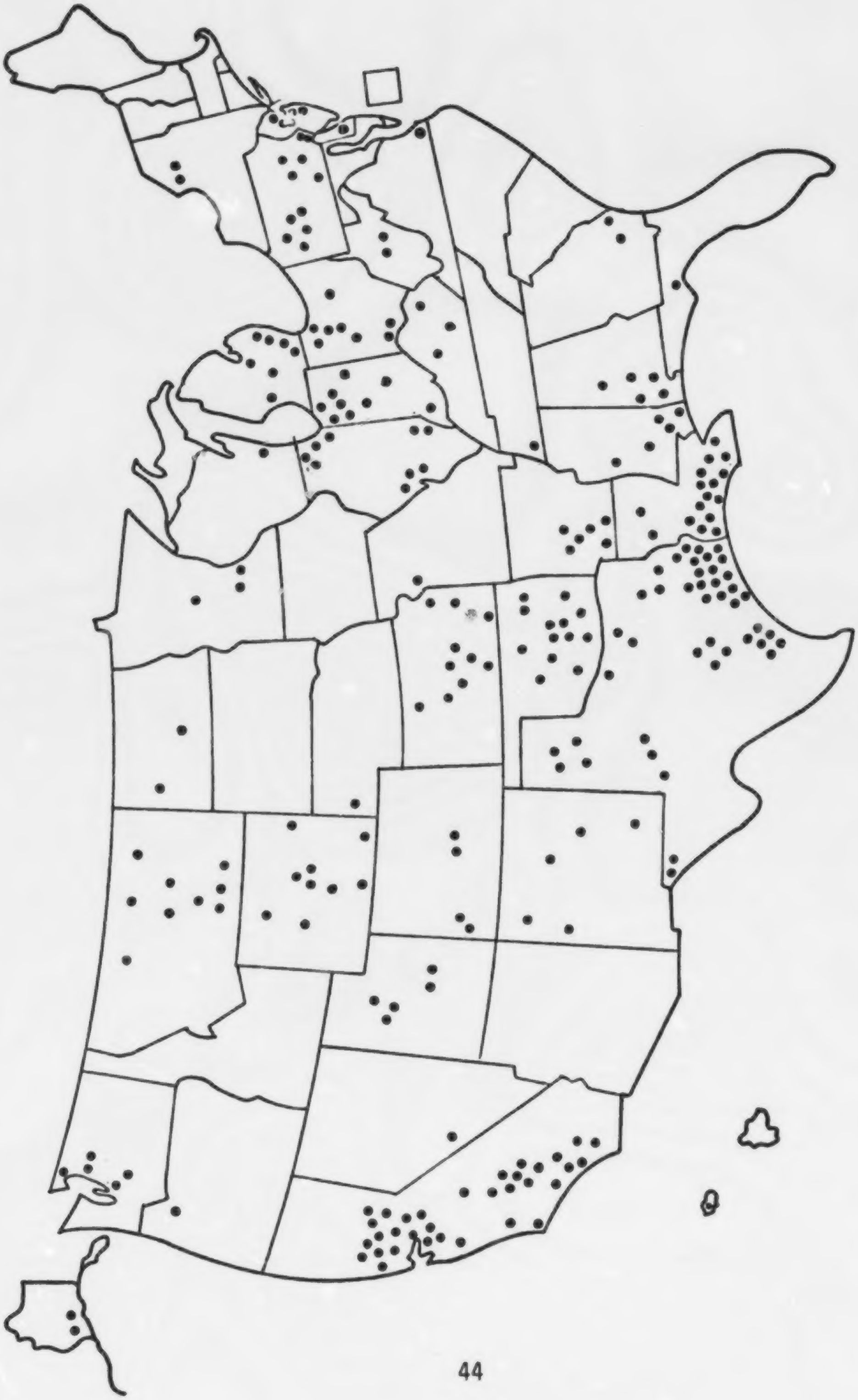
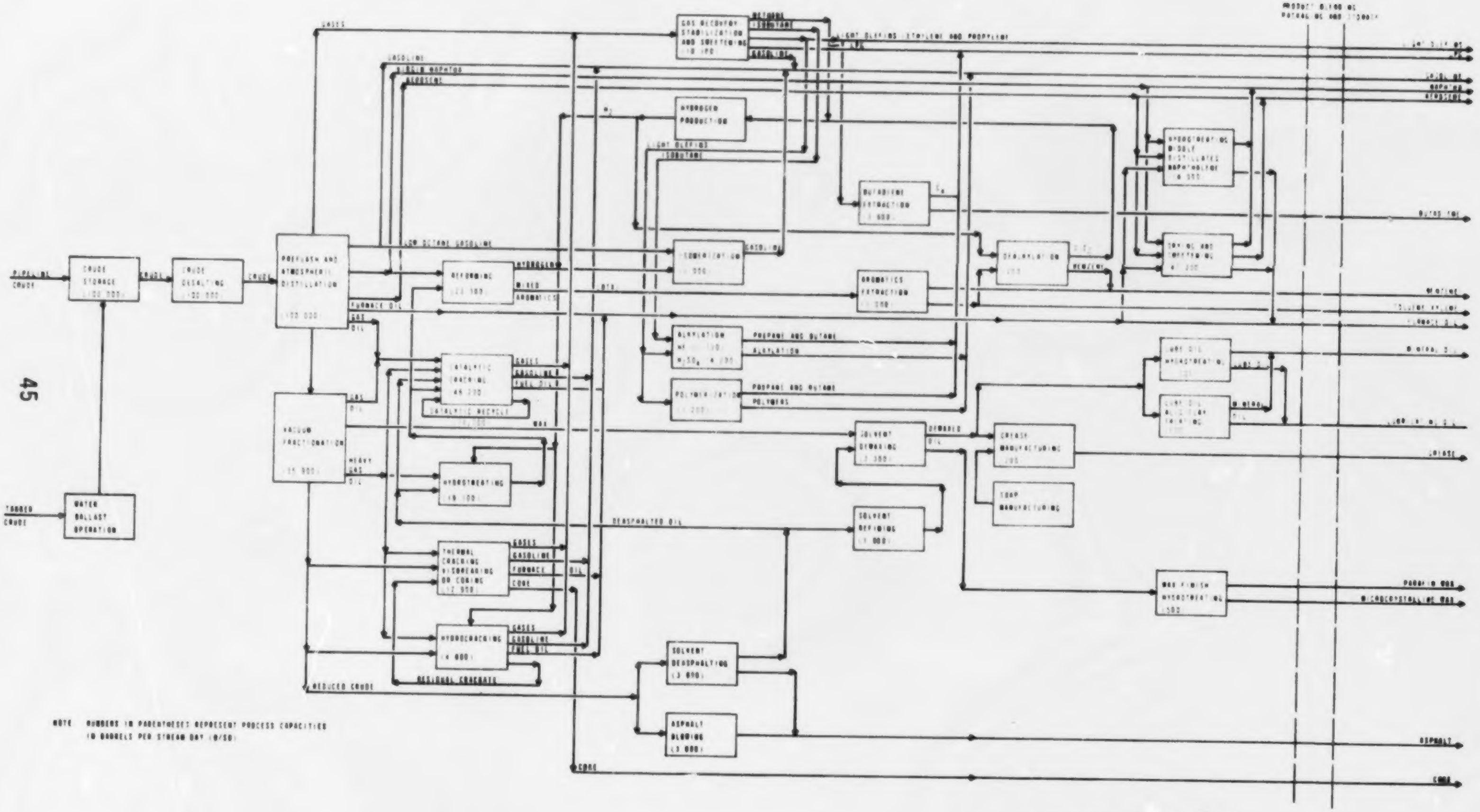


Figure 4
Geographical Distribution of Petroleum
Refineries in the
United States

FIGURE 5

HYPOTHETICAL 100,000 BARREL/STREAM DAY INTEGRATED REFINERY



NOTE: NUMBERS IN PARENTHESES REPRESENT PROCESS CAPACITIES IN BARRELS PER STREAM DAY (B/SD)

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TABLE 11

Process Employment Profile of Refining Processes as of January 1, 1973 (3)

Production Processes	Number of Refineries Employing a Production Process by Crude Capacity Classification				Percent of Refineries Employing a Production Process by Crude Capacity Classification			
	All Refineries	<35 MB/SD	35 to 100 MB/SD	>100 MB/SD	All Refineries	<35 MB/SD	35 to 100 MB/SD	>100 MB/SD
Storage: Crude & Product	247	141	65	41	100	100	100	100
Crude Desalting	247	141	65	41	100	100	100	100
Atmospheric Distillation	247	141	65	41	100	100	100	100
Vacuum Distillation	175	79	55	41	70	56	85	100
Thermal Cracking	87	27	32	28	35	19	49	68
Catalytic Cracking	141	41	59	41	57	29	91	100
Hydrocracking	45	11	11	23	18	8	17	56
Hydrotreating: Cat Reformer and Cat Crack Feed	129	42	52	35	52	30	80	85
Middle Distillates & Naptha	54	11	21	22	22	8	32	54
Lubes	13	2	2	9	5	1	3	22
Heavy Oils and Residuals	5	2	3	-	2	1	5	-
Other Feedstocks	57	14	17	26	23	10	26	63
Alkylation	125	30	57	38	51	21	88	93
Isomerization	30	4	19	7	12	3	29	17
Reforming	166	65	60	41	67	46	92	100
Aromatics	35	3	16	16	14	2	25	39
Lubes	44	16	10	18	18	11	15	44
Asphalt	111	58	30	23	45	41	46	56

TABLE 12

Trend in Domestic Petroleum Refining from 1967 to 1973 (3,3a)

	January 1, 1967	January 1, 1973	Percent Change
Crude Capacity, M^3/SD(bbl/SD)	1,853,618 (11,657,975)	2,224,661(13,991,580)	+ 20
Total Compnaies	146	132	(- 10)
Total Refineries	269	247	(- 8)
Refineries with Capacity __ 100 Mbbl/SD	31	41	+ 32
Refineries with Capacity 35 Mbbl/SD	159	141	(- 11)
Total Capacity of All Refineries 100 Mbbl/SD	5,597,300	8,167,200	+ 46
Average Refinery Capacity, M^3/SD (bbl/SD)	6890 (43,338)	9006(55,646)	+ 31

crude capacity in 1967; in 1972, 16.6 percent of the refineries had capacities of 15,900 cu m/day (100,000 bbl/day) or more, and represented 58 percent of the domestic refinery crude capacity. Growth of the large refinery was a result of the annual need for increased fuel capacity, and the imposed load due to the phasing out of smaller refineries. Refineries are increasing capacities for reforming, hydrotreating, cracking, and isomerization processes to obtain higher octane gasoline in lieu of adding lead. Desulfurization of heavy fuels, longer process catalyst life requirements, and high quality, low sulfur, light fuels and lubes are factors in the rapid growth of the hydrogen treating process. The complexity and size of the typical refinery can be expected to increase at a rate comparable to the period 1967 through 1972 for the near future, and no major technological breakthroughs are expected that would drastically alter petroleum processes.

Anticipated Industry Growth

The petroleum refining industry is presently facing a shortage of crude oil. There have been shortages of gasoline and fuel oil. Since demand continues to grow and little refinery expansion work is under way, shortages will become more severe over the next few years. Consumption of petroleum products will keep growing, and supplies must be generated to satisfy these growing demands. (1972 consumption of petroleum products, shown in Table 13, was approximately 2.56 million cu m/day (16.1 million bbl/day). The growth rate in consumption has been 5.2 percent per year; the projected growth in consumption over the next eight years is 43 percent, or a compounded growth rate of 4.6 percent per year.

Supplies of refinery feedstocks and products will show a rapid increase in imports. Table 14 indicates current and projected 1980 sources of feedstocks and products. In 1972, imports accounted for 29 percent of the total supply; in 1980, imports are projected at 55 percent of the total supply.

Refinery runs of crude oil are projected to increase from 1.86 million cu m/day (11.7 million bbl/day) in 1972 to 2.73 million cu m/day (17.2 million bbl/day) in 1980. Refinery capacity in 1972 was about 2.23 million cu m/day (14.0 million bbl/day). By 1980 the national refinery capacity must increase to 3.18 million cu m/day (20.0 million bbl/day) to satisfy the projected requirements. The need for 0.95 million cu m/day (6.0 million bbl/day) of new refinery construction for real growth, plus 0.64 million cu m/day (4.0 million bbl/day) of new construction for replacement, indicates a total of 1.59 million cu m/day (10.0 million bbl/day) of new refinery construction is required by 1980.

Because of crude supply limitations, most new refinery capacity will be designed to process higher sulfur crudes. (A partial list of analyses of crude oils from major oil fields around the world is given in Table 15.) The use of sour crude feedstock crude capacity in 1967; in 1972, 16.6 percent of the refineries had capacities of 15,900 cu m/day (100,000 bbl/day) or more, and represented 58 percent of the domestic refinery crude capacity. Growth of the large refinery was a result of the annual need for increased fuel capacity, and the imposed load due to the phasing out of smaller refineries. Refineries are increasing capacities for reforming, hydrotreating, cracking, and isomerization processes to obtain higher octane gasoline in lieu of adding lead. Desulfurization of heavy fuels, longer process catalyst life requirements, and high quality, low sulfur, light fuels and lubes are factors in the rapid growth of the hydrogen treating process. The complexity and size of the typical refinery can be expected to increase at a rate comparable to the period 1967 through 1972 for the near future, and no major technological breakthroughs are expected that would drastically alter petroleum processes.

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TABLE 13

1972 Consumption of Petroleum Products (63)

Products	1972 Consumption, Million Cubic Meters/Day (Million Barrels/Day
Motor Gasoline	1.02 (6.4)
Aviation Fuel	0.17 (1.1)
Middle Distillates	0.49 (3.1)
Residual Fuels	0.40 (2.5)
All Other Products	0.49 (3.1)

TABLE 14

Sources of Supply for U.S. Petroleum Feedstocks

Source	Supply, Million Barrels/Day	
	1972	1980 (Projected)
Domestic Crude Oil Production	9.5	8.5
Domestic Natural Gas Liquids	1.7	1.5
Crude Oil Imports	2.2	8.7
Residual Fuel Imports	1.7	2.5
Other Imports	0.8	1.5
Miscellaneous Sources	0.4	0.5

TABLE 15

Characteristics of Crude Oils from Major Fields Around the World (40, 43)

Country	Gravity, API	Sulfur, Percent	Nitrogen, Percent
Abu Dhabi	39.3		
Algeria	46 - 48	0.15	
Brunei	21 - 37	0.1	
Canada			
Alberta			
Bonnie Glen	41 - 42	0.25	
Golden Spike	36 - 39	0.23	
Judy Creek	42 - 43		
Pembina	35 - 42	0.42	
Swan Hills	41	0.80	
Saskatchewan			
Midale	28 - 32	1.89	
Weyburn	24 - 33	2.12	
Indonesia	35	0.10	
Iran	31 - 38	1.12 - 1.66	
Iraq	35 - 36	1.97	
Libya	37 - 41	0.23 - 0.52	
Mexico			
Ebano Panuco	12	5.38	
Naranjos-Cerro-Azul	20	3.80	
Poza Rica	35	1.77	
Peru	33.5 - 35.5	0.12	
Saudi Arabia	27 - 38	1.30 - 3.03	
United States			
Alaska			
Cook Inlet	36	0.0	
Prudhoe Bay	30.5		
Swanson River	29.7	0.16	0.203
Arkansas			
Smackover	22.2	2.10	0.080

TABLE 15
(Continued)

Country	Gravity, API	Sulfur, Percent	Nitrogen, Percent
California			
Elk Hills	22.5	0.68	0.472
Huntington Beach	22.6	1.57	0.048
Kern River	12.6	1.19	0.604
Midway-Sunset	22.6	0.94	
San Ardo	11.1	2.25	0.913
Wilmington	22.1	1.44	
Colorado			
Rangely	34.8	0.56	0.073
Kansas			
Bemis Shutts	34.6	0.57	0.162
Louisiana			
Bayou Sale	36.2	0.16	
Caillou Isl.	35.4	0.23	0.040
Golden Meadow	37.6	0.18	
Grand Bay	35	0.31	
Lake Barre	40.4	0.14	0.02
Lake Washington	28.2	0.37	0.146
West Bay	32.1	0.27	0.071
Bay Marchand Blk. 2	20.2	0.46	
Main Pass Blk. 69	30.6	0.25	0.098
South Pass Blk. 24	32.3	0.26	0.068
South Pass Blk. 27	35.6	0.18	0.069
Timbalier Bay	34.4	0.33	0.081
West Delta Blk. 30	27	0.33	0.09
Mississippi			
Baxterville	17.1	2.71	0.111
New Mexico			
Vacuum	35	0.95	0.075
Oklahoma			
Golden Trend	42.1	0.11	
Texas			
Anahuac	33.2	0.23	0.041
Conroe	37.6	0.15	
Diamond M	45.4	0.20	
East Texas	39.4	0.32	
Hastings	31.0	0.15	0.02
Hawkins	26.8	2.19	0.076
Headlee	51.1	<0.10	0.083
Kelly Snyder	38.6	0.29	0.066
Levelland	31.1	2.12	0.136
Midland Farms	39.6	0.13	0.080
Panhandle	40.4	0.55	0.067
Seeliason	41.3	<0.10	0.014

TABLE 15
(Continued)

Country	Gravity, API	Sulfur, Percent	Nitrogen, Percent
Tom O'Connor	31.1	0.16	0.03
Wasson	31.9	1.40	0.07
Webster	29.3	0.21	0.046
Yates	30.2	1.54	0.150
Utah			
Aneth	40.4	0.20	0.059
Venezuela			
Bachaquero	21.3	2.62	
Boscan	10.5	5.53	
Lagunillas	24.8	2.18	
Mene Grande	18.4	2.65	
Tia Juana	20.2	1.49	
Oficina	21.4	0.59	
Los Claros	10.5		

from outside the United States will require not only a change in processing equipment, but changes in in-plant waste water control and treatment operations. Some refineries currently consuming sweet crude stocks are not employing strippers to remove minimal amounts of ammonia and hydrogen sulfide from their waste waters. When processing sour crude within these refineries, sour water strippers will be required prior to discharge of the waste waters to biological waste water treatment facilities. Two stage desalting will become more prevalent. Other changes will be required within the refinery to minimize corrosion, treat more sour heavy bottoms, and reduce emissions of sour gases.

SECTION IV

INDUSTRY SUBCATEGORIZATION

Discussion of the Rationale of Subcategorization

The goal of this study is the development of effluent limitations commensurate with different levels of pollution control technology. These effluent limitations will specify the quantity of pollutants which will ultimately be discharged from a specific manufacturing facility and will be related to the quantity of raw materials consumed and the production methodology.

The diverse range of products and manufacturing processes to be covered suggests that separate effluent limitations be designated for different segments within the industry. To this end, a subcategorization of the Petroleum Refining Industry has been developed. The subcategorization is process oriented, with a delineation between subcategories based upon raw waste load characteristics in relation to the complexity of refinery operations.

Today's petroleum refinery is a very complex combination of interdependent operations and systems. In the development of a pollution profile for this industry, ten major process categories were listed as fundamental to the production of principal oil products (see listing in Table 8).

The American Petroleum Institute (API) has developed a classification system which utilizes this technology breakdown. They have tentatively divided U.S. refineries into 5 classifications, which primarily recognize varying degrees of processing complexity and resultant distribution of products. The present API classification system is as follows:

Class	Process Complexity
A	Crude Topping
B	Topping and Cracking
C	Topping, cracking, and petrochemicals
D	"B" Category, and lube oils processing
E	"D" Category, and petrochemicals

Development of Industry Subcategorization

Age, size, and waste water treatability of refineries were considered during the subcategorization of the refining industry. However, subcategorization by age is not necessarily useful, as additions to and modifications of refineries are the industry's principal form of expansion. Since most of the technology employed within the industry is of an evoluationary nature, refinery age was not a major factor in refinery subcategorization.

While the size of a refinery is important in terms of economical waste water treatment, the control technology employed in smaller refineries need not be as sophisticated a technology to achieve parity with larger refineries within the same subcategory.

Treatability characteristics of refinery waste waters indicate that these waste waters are generally amenable to excellent degrees of removal of pollutants. Since this is an industry-wide characteristic, the proper place to evaluate the subcategorization of the industry is with the raw waste load delivered to the refinery waste water treatment plant. The 1972 National Petroleum Refining Waste Water Characterization Studies of 135 refinery API separator effluents, provides a major tool for this evaluation. Attempts to explain and justify the differences based solely on type and method of cooling, inplant pretreatment, and housekeeping practices were also fruitless. However, generally speaking those refineries with good practices in all these areas did have the lower waste loadings.

In an attempt to determine the effects of process technology, a further analysis was made of the API individual or combined categories to evaluate the raw waste load as a function of the degree of cracking employed within the refinery. The operations included in degree of cracking were: thermal operations, catalytic cracking and hydroprocessing. The degree of cracking was expressed as percentage capacity of the total feedstock processing capacity within the refinery. The data for evaluating the net raw waste loads by this criteria were obtained by analyzing the raw waste load surveys supplied by refineries, literature sources, and analysis of the 1972 National Petroleum Refining Waste Water Characterization Studies.

Even though this new breakdown was a step in the right direction it did not explain raw waste load differences caused by the amount of cracking in the other subcategories and did not explain the effect of other process on the raw waste load. Therefore, the effort to further determine the effect of each refining process on the raw waste load continued.

Since the guideline is based on attainable flow rates and achievable concentrations based on each treatment technology, the effort was directed toward determining the relative flows expected from the many refining processes.

The approach taken, was the use of a multiple regression analysis using process and flow data from the 1972 National Petroleum Refining Waste Water Characterization Studies. The data consisted of waste water flows and individual process capacities for 94 refineries with less than 3 percent heat removal by once-through cooling. Those refineries with greater than 3 percent once-through cooling water were not used in order to eliminate as much of the non-process flow variation as possible.

The initial regressions carried out were in the form:

$$(1)\quad \frac{\text{Total Flow}}{\text{Capacity}} = A + B \,\varepsilon\, \text{Ci Pi}$$

where A,B,and C are the constants to be determined from the regressions; Pi is the capacity of individual process categories relative to the refinery throughput and for each Pi there is a Ci which is the relative "weight" or importance of each process category in explaining the flow. The initial process breakdown used was supplied through the American Petroleum Institute and broke 126 individual process types into nine process categories.

Since the results of this initial form were not considered satisfactory, attempts were made to find out what other factors, if any, had explanatory power in predicting refinery flow. After many attempts, it was found that in addition to the process configuration of the refinery, the refinery size was an important factor in explaining the flow.

The final form of the equation which gave the best fit to the data was as follows:

$$(2)\quad \log \frac{\text{Total Flow}}{\text{Capacity(T)}} = A + BT + C \,\varepsilon\, \text{Di Pi}$$

where T or capacity is equal to the refinery throughput; A, C, Di and Pi are the same as A, B, Ci and Pi, respectively, in the initial regression form; and B is a constant.

Adjustments were then made to the API breakdown of the process categories to improve the fit to the data. The 126 individual processes were finally put into one of the following nine process categories:

1. crude processes
2. cracking processes
3. hydrocarbon processing
4. lubes and greases
5. coking processes
6. treating and finishing processes
7. first generation petrochemicals
8. second generation petrochemicals
9. asphalt production

It was found that only crude processes, cracking processes, lubes and greases, coking processes, second generation petrochemicals and asphalt production showed significance in the regression. In addition, even though second generation petrochemicals showed significance, the Di or "weighting factor" for it was -6. The nonsignificant processes and second generation petrochemicals were therefore given 0 (zero) weighting factors.

The Di's or weighting factors for the significant process categories are as follows: crude process +1; cracking and coking processes +6; lubes and greases +13; and asphalt production +12.

A breakdown of the individual process in each process category is contained in Table 51.

The values for constants B and C were then obtained by regressing against flow with equation (2) with the Di value defined as above. The resulting values are B=1.51 and C=0.0738. The magnitude of A has no significance since the analysis is to be used only within each subcategory and not across all subcategories. (Fitting the actual flows with those predicted was tried both using the analysis across the entire industry and within each subcategory, with the results being much better using it only to explain differences within subcategories).

The above results were then put into a usable form by taking the anti log of equation (2), which is

$$\text{(3)}\quad \text{flow(gal/bbl)} = A10^{BT}\ 10^{C\ \mathcal{E}\,DiPi}$$

The constant A is now the 50 percent probability flow (gal/bbl) which was used previously to calculate the limits for each subcategory. To apply this to each subcategory (to determine the variance needed for each case from the average refinery in each subcategory) the average size (Ta) and process configuration ([$\mathcal{E}$ DiPi]a) for each subcategory was calculated. The range of sizes and process configurations were then divided up into ranges and the midpoint of each range was then compared to the average for that subcategory to calculate the size and process factor for that range (see below).

$$10^{BT} = 10^{1.51(Ti-Ta)}$$

$$10^{C\ \mathcal{E}\,DiPi} = 10^{0.0738[(\mathcal{E}\,DiPi)j-(\mathcal{E}\,DiPi)a]}$$

where Ti is the midpoint of that particular size range; Ta is the average size in the subcategory, with both Ta and Ti in millions of barrells per day; [$\mathcal{E}$ DiPi]i is the midpoint of that particular process configuration range; and [$\mathcal{E}$ DiPi]a is the average process configuration of the subcategory.

Further analysis of the data showed a break in the significance of size in explaining flow for those refineries over 150,000 bbl/day. This means that over 150,000 bbl/day only the process configuration has significance in explaining the flows. As a result the size ranges where broken off at either 150,000 bbl/day or the average refinery size in a subcategory, whichever was greater.

An example of the application of the size and process factors is in section IX. The basic data used, regressions run, etc. are in Supplement B "Refinery Configuration Analysis".

The size and process factors are in Table 1 - 5, Section II.

Subcategorization Results

Using the procedures outlined above, many trials were performed in order to obtain a subcategorization of the petroleum refining industry which is reflective of the net raw waste load with respect to type of refinery (function), process technology employed, and severity of operations. The final subcategorization obtained from this analysis is indicated below in Table 16. Detailed probability plots for the development of the subcategorization are contained in supplement B.

For each of these new subcategories the parameters for the selected median values are indicated in Table 17. A further enumeration of overall net raw waste load characteristics is given in Section V.

Analysis of the Subcategorization

Topping subcategory

The topping subcategory is similar to the previous API category A in that it does not include any refineries with cracking or coking processes. That is to say it includes all refineries which combine all other porcesses except cracking and coking.

Cracking subcategory

API Category B includes refineries which contain topping, reforming, and cracking operations. Also included are all first generation conventional refinery-associated products or intermediates, such as benzene-toluene-xylene (BTX), alkanes, alkenes, alkynes, and other miscellaneous items such as sulfur, hydrogen and coke.

Subcategory B as defined here is the same as API category B execpt that the inclusion of first generation petrochemicals shall only be for those whose production amounts to less than 15 percent of the refinery throughput.

Petrochemical subcategory

The petrochemical subcategory is similar to the API category C. Operations included within this subcategory are topping,

TABLE 16

Subcategorization of the Petroleum Refining Industry Reflecting Significant Differences in Waste Water Characteristics

Subcategory	Basic Refinery Operations Included
Topping	Topping and catalytic reforming whether or not the facility includes any other process in addition to topping and catalytic process. This subcategory is not applicable to facilities which include thermal processes (coking, visbreaking, etc.) or catalytic cracking.
Cracking	Topping and cracking, whether or not the facility includes any processes in addition to topping and cracking, unless spefified in one of the subcategories listed below.
Petrochemical	Topping, cracking and petrochemical operations, whether or not the facility includes any process in addition to topping, cracking and petrochemical operations,* except lube oil manufacturing operations.
Lube	Topping, cracking and lube oil manufacturing processes, whether or not the facility includes any process in addition to topping, cracking and lube oil manufacturing processes, except petrochemical operations.*
Integrated	Topping, cracking, lube oil manufacturing processes, and petrochemical operations, whether or not the facility includes any processes in addition to topping, cracking, lube oil manufacturing processes and petrochemical operations.*

* The term "petrochemical operations" shall mean the production of second generation petrochemicals (i.e., alcohols, ketones, cumene, styrene, etc.) or first generation petrochemicals and isomerization products (i.e., BTX, olefins, cyclohexane, etc.) when 15% or more of refinery production is as first generation petrochemicals and isomerization products.

TABLE 17

NET RAW WASTE LOADS FROM PETROLEUM REFINING INDUSTRY CATEGORIES (50 Percent Probability of Occurrence)

KILOGRAMS/10000 M^3 (LB/1000 BBLS)

SUBCATEGORY	BOD5	OIL/GREASE	PHENOL	AMMONIA
TOPPING	3.43(1.2)	8.29(2.9)	0.034(0.012)	1.20(0.42)
CRACKING	72.93(25.5)	31.17(10.9)	4.00(1.4)	28.31(9.9)
PETROCHEMICAL	171.6(60)	52.91(18.5)	7.72(2.7)	34.32(12)
LUBE	217(76)	120.1(42)	8.3(2.9)	24.1(8.5)
INTEGRATED	197(69)	75(26)	3.8(1.3)	20.5(7.2)

cracking, and petrochemical operations. Petrochemical operations include first generation conventional refinery-associated production, as described in the cracking subcategory, but only when it amounts to greater than 15 percent of the refinery throughput. This takes into consideration the additional cooling tower blowdown from this operation. Intermediate chemical production, including such typical products as cumene, phthalic anhydride, alcohols, ketones, trimer, and styrene, shall be considered second generation petrochemical operations and classify a refinery in this subcategory.

Lube subcategory

The lube subcategory is the same as the API category D.

In the lube subcategory, the operations included under the cracking subcategory are expanded to include lube oil manufacturing processes. Lube oil processing excludes formulating blended oils and additives.

Integrated subcategory

The integrated subcategory is the same as API category E, except for the definition of petrochemical operatons specified in the petrochemical subcategory.

Conclusion

The subcategorization of the petroleum refinery industry presented above allows for the definition of logical segments of the industry in terms of factors which effect generated API separator effluent waste water quality. It allows for rapid identification of the expected median net raw waste loads as a basis for developing effluent guidelines for the discharge from the individual refinery. The subcategorization determined above is used throughout this report as the basis for development of effluent limitations and guidelines.

SECTION V

WASTE CHARACTERIZATION

General

After developing an understanding of the fundamental production processes and their inter-relationships in refinery operations, determination of the best method of characterizing of refinery discharges will enhance the interpretation of the industry water pollution profile. If unit raw waste loads could be developed for each production process, then the current effluent waste water profile could be obtained by simply adding the components, and future profiles by projecting the types and sizes of refineries. However, the information required for such an approach is not available. Essentially all of the available data on refinery waste waters apply to total API separator effluent, rather than to effluents from specific processes.

Another factor detracting from the application of a summation of direct subprocess unit raw waste loads, is the frequent practice of combining specific waste water streams discharging from several units for treatment and/or reuse. Thus, such streams as sour waters, caustic washes, etc., in actual practice are generally not traceable to a specific unit, but only to a stripping tower or treatment unit handling wastes from several units. The size, sequence, and combination of contributing processes are so involved that a breakdown by units would be extremely difficult to achieve.

In view of the limitations imposed by the summation of waste water data from specific production process, the evaluation of refinery waste loads was based on total refinery effluents discharged through the API (Oil) separator, which is considered an integral part of refinery process operations for product/raw material recovery prior to final waste water treatment.

Raw Waste Loads

The information on raw waste loading was compiled from the 1972 National Petroleum Refining Waste Water Characterization Studies and plant visits. The data are considered primary source data, i.e., they are derived from field sampling and operating records. The raw waste data for each subcategory of the petroleum refining industry, as subcategorized in Section IV, have been analyzed to determine the probability of occurrence of mass loadings for each considered parameter in the subcategory. These frequency distributions are summarized in Tables 18 through 22 for each subcategory.

Waste water Flows

As shown in Table 18 through 22, the waste water flows associated with raw waste loads can vary significantly. However, the

TABLE 18

TOPPING SUBCATEGORY RAW WASTE LOAD**
EFFLUENT FROM REFINERY API SEPARATOR

NET KILOGRAMS/1000 M^3 (LB/1000 BBLS) OF FEEDSTOCK
THROUGHPUT

PARAMETER	PROBABILITY OF OCCURRENCE PERCENT LESS THAN OR EQUAL TO		
	10%	50%(MEDIAN)	90%
BOD_5	1.29(0.45)	3.43(1.2)	217.36(76)
COD	3.43(1.2)	37.18(13)	486.2(170)
TOC	1.09(0.38)	8.01(2.8)	65.78(23)
TSS	0.74(0.26)	11.73(4.1)	286(100)
O&G	1.03(0.36)	8.29(2.9)	88.66(31)
PHENOLS	0.001(0.0004)	0.034(0.012)	1.06(0.37)
AMMONIA	0.077(0.027)	1.20(0.42)	19.45(6.8)
SULFIDES	0.002(0.00065)	0.054(0.019)	1.52(0.53)
CHROMIUM	0.0002(0.00007)	0.007(0.0025)	0.29(0.1)
FLOW*	8.00(2.8)	66.64(23.3)	557.7(195)

* 1000 cubic meters/1000 m^3 Feedstock Throughput (gallons/bbl)
** Probability plots are contained in Supplement B

TABLE 19

CRACKING SUBCATEGORY RAW WASTE LOAD** EFFLUENT FROM REFINERY API SEPARATOR

NET KILOGRAMS/1000 M^3 (LB/1000 BBLS) OF FEEDSTOCK THROUGHPUT

PARAMETER	PROBABILITY OF OCCURRENCE PERCENT LESS THAN OR EQUAL TO		
	10%	50%(MEDIAN)	90%
BOD_5	14.3(5.0)	72.93(25.5)	466.18(163)
COD	27.74(9.7)	217.36(76.0)	2516.8(880)
TOC	5.43(1.9)	41.47(14.5)	320.32(112)
O&G	2.86(1.0)	31.17(10.9)	364.65(127.5)
PHENOLS	0.19(0.068)	4.00(1.4)	80.08(28.0)
TSS	0.94(0.33)	18.16(6.35)	360.36(126.0)
SULPHUR	0.01(0.0035)	0.94(0.33)	39.47(13.8)
CHROMIUM	0.0008(0.00028)	0.25(0.088)	4.15(1.45)
AMMONIA	2.35(0.82)	28.31(9.9)	174.46(61.0)
FLOW*	3.29(1.15)	92.95(32.5)	2745.6(960.0)

* 1000 cubic meters/1000 m^3 Feedstock Throughput (gallons/bbl)

** Probability plots are contained in Supplement B

TABLE 20

PETROCHEMICAL SUBCATEGORY RAW WASTE LOAD**
EFFLUENT FROM REFINERY API SEPARATOR

NET KILOGRAMS/1000 M^3 (LB/1000 BBLS) OF FEEDSTOCK THROUGHPUT

PARAMETER	PROBABILITY OF OCCURRENCE PERCENT LESS THAN OR EQUAL TO		
	10%	50%(MEDIAN)	90%
BOD5	40.90(14.3)	171.6(60)	715(250)
COD	200.2(70)	463.32(162)	1086.8(380)
TOC	48.62(17)	148.72(52)	457.6(160)
TSS	6.29(2.2)	48.62(17)	371.8(130)
O&G	12.01(4.2)	52.91(18.5)	234.52(82)
PHENOLS	2.55(0.89)	7.72(2.7)	23.74(8.3)
AMMONIA	5.43(1.9)	34.32(12)	205.92(72)
SULFIDES	0.009(0.003)	0.86(0.3)	91.52(32)
CHROMIUM	0.014(0.005)	0.234(0.085)	3.86(1.35)
FLOW*	26.60(9.3)	108.68(38)	443.3(155)

* 1000 cubic meters/1000 m^3 Feedstock Throughout (gallons/bbl)

** Probability plots are contained in Supplement B

TABLE 21

LUBE SUBCATEGORY RAW WASTE LOAD**
EFFLUENT FROM REFINERY API SEPARATOR

NET KILOGRAMS/1000 M^3 (LB/1000 BBLS) OF FEEDSTOCK
THROUGHPUT

PARAMETERS	PROBABILITY OF OCCURRENCE PRECENT LESS THAN OR EQUAL TO		
	10%	50%(MEDIAN)	90%
BOD_5	62.92(22)	217.36(76)	757.9(265)
COD	165.88(58)	543.4(190)	2288(800)
TOC	31.46(11)	108.68(38)	386.1(135)
TSS	17.16(6)	71.5(25)	311.74(109)
O&G	23.74(8.3)	120.12(42)	600.6(210)
PHENOLS	4.58(1.6)	8.29(2.9)	52.91(18.5)
AMMONIA	6.5(2.3)	24.1(8.5)	96.2(34)
SULFIDES	0.00001(0.000005)	0.014(0.005)	20.02(7.0)
CHROMIUM	0.002(0.0006)	0.046(0.016)	1.23(0.43)
FLOW*	68.64(24)	117.26(41)	772.2(270)

* 1000 cubic meters/1000 m^3 Feedstock Throughput (gallons/bbl)
** Probability plots are contained in Supplement B

TABLE 22

INTEGRATED SUBCATEGORY RAW WASTE LOAD**
EFFLUENT FROM REFINERY API SEPARATOR

NET KILOGRAMS/1000 M^3 (LB/1000 BBLS) OF FEEDSTOCK THROUGHPUT

PARAMETERS-	PROBABILITY OF OCCURRENCE PERCENT LESS THAN OR EQUAL TO		
	10%	50%(MEDIAN)	90%
BOD5	63.49(22.2)	197.34(69.0)	614.9(215)
COD	72.93(25.5)	328.9(115)	1487.2(520)
TOC	28.6(10.0)	139.0(48.6)	677.82(237)
O&G	20.88(7.3)	74.93(26.2)	268.84(94.0)
PHENOL	0.61(0.215)	3.78(132)	22.60(7.9)
TSS	15.16(5.3)	58.06(20.3)	225.94(79.0)
SULPHUR	0.52(.182)	2.00(.70)	7.87(2.75)
CHROMIUM	0.12(0.043	0.49(0.17)	1.92(0.67
AMMONIA	3.43(1.20)	20.50(7.15)	121.55(42.5)
FLOW*	40.04(14.0)	234.52(82.0)	1372.8(480)

* 1000 cubic meters/1000 m^3 Feedstock Throughput (gallons/bbl)
** Probability plots are contained in Supplement B

loadings of pollutants tend to vary within fairly narrow limits, independent of flow.

Since the inter-refinery data suggest that the pollutant loading to be expected from a refinery is relatively constant in concentration, an examination of water use practices was made. The waste water flow frequencies reported in Tables 18 through 22 are dry-weather flows, and in many cases include large amounts of once-through cooling water. Refineries with more exemplary waste water treatment systems are probably making a greater effort to control waste loads and flows. Conversely, refineries with very high water usages and/or raw waste loads either do not have identifiable waste water treatment plants, or have them under construction.

The primary methods for reduction of the waste water flows to the API separator are either segregation of once-through cooling waters, or by installation of recycle cooling towers and/or air coolers. In order to estimate the flows that should be attainable in refineries with good water practices, a statistical analysis was made of flows from refineries in which 3 percent or less of the total heat removal load is accomplished by once-through cooling water. Data for this analysis were obtained from the tabulation of refinery cooling practices contained in the 1972 National Petroleum Refining Waste Water Characterization Studies. These frequency distributions are summarized in Table 23.

Basis for Effluent Limitations

The 50 percent probability-of-occurrence raw waste loads outlined in Tables 18 through 22 are reflective of the performance of median refineries within each subcategory. At the same time, attainable process waste water flows, as reflected by the median water usage for refineries in which 3 percent or less of the total heat removal load is accomplished by once-through cooling water, are indicative of equitable process waste water loadings which require waste water treatment.

Consequently, these 50 percent probability-of-occurrence waste water loadings and estimated process waste water flows were selected as one basis for developing effluent limitations, and are used in subsequent sections to define these effluent limitations.

TABLE 23

WASTE WATER FLOW FROM PETROLEUM REFINERIES USING 3% OR LESS ONCE-THROUGH COOLING WATER FOR HEAT REMOVAL*

KILOGRAMS/1000 M^3 (LB/1000 BBLS) OF FEEDSTOCK THROUGHPUT

SUBCATEGORY	PROBABILITY OF OCCURRENCE PERCENT LESS THAN OR EQUAL TO		
	10%	50%(MEDIAN)	90%
TOPPING	8.01(2.8)	57.2(20)	314.6(110)
CRACKING	16.59(5.8)	71.5(25)	148.72(52)
PETROCHEMICAL	40.04(14)	85.8(30)	183.04(64)
LUBE	65.78(23)	128.7(45)	243.1(85)
INTEGRATED	91.52(32)	137.28(48)	1287(450)

* Probability plots are contained in Supplement B

SECTION VI

SELECTION OF POLLUTANT PARAMETERS

Selected Parameters

The selection of the complete list of pollutant parameters which are discharged in significant quantities was based on a review of: the Environmental Protection Agency permits for discharge of waste waters from a number of refineries; reviews with personnel in regional EPA offices; the 1972 National Petroleum Refining Waste Water Characterization Studies; discussions with industry representatives and consultants; and literature survey data. The results of the above indicated the parameters shown in Table 24 are significant in describing the physical, chemical and biological characteristics of waste waters discharged by the petroleum refining industry, as defined in the Act.

The rationale and justification for inclusion of these parameters are discussed below. This discussion will provide the basis for selection of parameters upon which the actual effluent limitations were postulated and prepared. In addition, particular parameters were selected for discussion in the light of current knowledge as to their limitations from an analytical as well as from an environmental standpoint.

Oxygen Demand Parameters

Three oxygen demand parameters are discussed below: BOD5, COD, and TOC. It should be noted that limitations are specified for BOD5, COD, and TOC in sections IX, X, and XI for each subcategory.

Almost without exception, waste waters from petroleum refineries exert a significant and sometimes major oxygen demand. The primary sources are soluble biodegradable hydrocarbons and inorganic sulfur compounds. Crude distillation, cat cracking, and the product finishing operations, are the major contributors of BOD5. In addition, the combination of small leaks and inadvertent losses that occur almost continuously throughout a complex refinery can become principal BOD5 pollution sources.

Biochemical oxygen demand (BOD) is a measure of the oxygen consuming capabilities of organic matter. The BOD does not in itself cause direct harm to a water system, but it does exert an indirect effect by depressing the oxygen content of the water. Sewage and other organic effluents during their processes of decomposition exert a BOD, which can have a catastrophic effect on the ecosystem by depleting the oxygen supply. Conditions are reached frequently where all of the oxygen is used and the continuing decay process causes the production of noxious gases such as hydrogen sulfide and methane. Water with a high BOD indicates the presence of decomposing organic matter and

TABLE 24

Significant Pollutant Parameters for the Petroleum Refining Industry

Biochemical Oxygen Demand (BOD5)

Chemical Oxygen Demand (COD)

Total Organic Carbon (TOC)

Oil and Grease (O&G)

Ammonia as Nitrogen (NH3-N)

Phenolic Compounds

Sulfides

Chromium

subsequent high bacterial counts that degrade its quality and potential uses.

Dissolved oxygen (DO) is a water quality constituent that, in appropriate concentrations, is essential not only to keep organisms living but also to sustain species reproduction, vigor, and the development of populations. Organisms undergo stress at reduced DO concentrations that make them less competitive and able to sustain their species within the aquatic environment. For example, reduced DO concentrations have been shown to interfere with fish population through delayed hatching of eggs, reduced size and vigor of embryos, production of deformities in young, interference with food digestion, acceleration of blood clotting. decreased tolerance to certain toxicants, reduced food efficiency and growth rate, and reduced maximum sustained swimming speed. Fish food organisms are likewise affected adversely in conditions with suppressed DO. Since all aerobic aquatic organisms need a certain amount of oxygen, the consequences of total lack of dissolved oxygen due to a high BOD can kill all inhabitants of the affected area.

If a high BOD is present, the quality of the water is usually visually degraded by the presence of decomposing materials and algae blooms due to the uptake of degraded materials that form the foodstuffs of the algal populations.

Historically, the BOD5 test has also been used to evaluate the performance of biological waste water treatment plants and to establish effluent limitation values. However, objections to the use of the BOD5 test have been raised.

The major objections are as follows:

1. The standard BOD5 test takes five days before the results are available, thereby negating its use as a day-to-day treatment plant operational indicator.

2. At the start of the BOD5 test, seed culture (microorganisms) is added to the BOD5 bottle. If the seed culture was not acclimated, i.e., exposed to a similar waste water in the past, it may not readily be able to biologically degrade the waste. This results in the reporting of a low BOD5 value. This situation is very likely to occur when dealing with complex industrial wastes, for which acclimation is required in most cases. The necessity of using "acclimated bacteria" makes it very important to take a seed from the biological plant treating the waste or downstream of the discharge in the receiving waterbody.

3. The BOD5 test is sensitive to toxic materials, as are all biological processes. Therefore, if toxic materials are present in a particular waste water, the reported BOD5 value may very well be erroneous. This situation

can be remedied by running a toxicity test, i.e., subsequently diluting the sample until the BOD5 value reaches a plateau indicating that the material is at a concentration which no longer inhibits biological oxidation.

There has been much controversy concerning the use of BOD5 as a measure of pollution, and there have been recommendations to substitute some other parameter, e.g., COD or TOC. EPA has recently pointed out that some or all of the previously cited reasons make the BOD5 test a non-standard test, and ASTM's Subcommittee D-19 has also recommended withdrawal of the BOD5 test as a standard test.

However, some of the previously cited weaknesses of the BOD5 test also make it uniquely applicable. It is the only parameter now available which measures the amount of oxygen used by selected microorganisms in metabolizing a waste water. The use of COD or TOC to monitor the efficiency of BOD5 removal in biological treatment is possible only if there is a good correlation between COD or TOC and BOD. After consideration of the advantages, disadvantages and constraints, BOD5 will continue to be used as a pollutional indicator for the petroleum refining industry.

Typical raw waste load concentrations for each subcategory are listed below:

Subcategory	BOD5 RWL Range, mg/l
Topping	10 - 50
Cracking	30 - 600
Petrochemical	50 - 800
Lube	100 - 700
Integrated	100 - 800

As a matter of reference, typical BOD5 values for raw municipal waste waters range between 100 and 300 mg/L.

COD

Chemical oxygen demand (COD) provides a measure of the equivalent oxygen required to oxidize the materials present in a waste water sample, under acid conditions with the aid of a strong chemical oxidant, such as potassium dischromate, and a catalyst (silver sulfate). One major advantage of the COD test is that the results are available normally in less than three hours. Thus, the COD test is a faster test by which to estimate the maximum oxygen exertion demand a waste can make on a stream. However, one major disadvantage is that the COD test does not differentiate between biodegradable and non-biodegradable organic material. In addition, the presence of inorganic reducing chemicals (sulfides, reducible metallic ions, etc.) and chlorides may interfere with the COD test.

The slow accumulation of refractory (resistant to biological decomposition) compounds in watercourses has caused concern among various environmentalists and regulatory agencies. However, until these compounds are identified, analytical procedures developed to quantify them, and their effects on aquatic plants and animals are documented, it may be premature (as well as economically questionable) to require their removal from waste water sources.

Typical raw waste load concentrations for each subcategory are listed below:

Subcategory	COD RWL Range, mg/l
Topping	50 - 150
Cracking	150 - 400
Petrochemical	300 - 600
Lube	400 - 700
Integrated	300 - 600

Typical COD values for raw municipal waste waters are between 200 mg/l and 400 mg/l.

TOC

Total organic carbon (TOC) is a measure of the amount of carbon in the organic material in a waste water sample. The TOC analyzer withdraws a small volume of sample and thermally oxidizes it at 150°C. The water vapor and carbon dioxide from the combustion chamber (where the water vapor is removed) is condensed and sent to an infrared analyzer, where the carbon dioxide is monitored. This carbon dioxide value corresponds to the total inorganic value. Another portion of the same sample is thermally oxidized at 950°C, which converts all the carbonaceous material to carbon dioxide; this carbon dioxide value corresponds to the total carbon value. TOC is determined by subtracting the inorganic carbon (carbonates and water vapor) from the total carbon value.

The recently developed automated carbon analyzer has provided a rapid and simple means of determining organic carbon levels in waste water samples, enhancing the popularity of TOC as a fundamental measure of pollution. The organic carbon determination is free of many of the variables which plague the COD and BOD analyses, yielding more reliable and reproducible data. However, meaningful correlations between the three are sometimes hard to develop.

Typical raw waste concentrations for each subcategory are presented below:

Subcategory	TOC RWL Range, mg/l
Topping	10 - 50
Cracking	50 - 500
Petrochemical	100 - 250
Lube	100 - 400
Integrated	50 - 500

Typical values for raw municipal waste waters range between 50 and 250 mg/L.

TSS

In refineries, major sources of suspended matter are contributed by crude storage, alkylation, crude desalting and finishing operations. Quenching and removal operations in the production of coke can contribute significant amounts of suspended fines to the refinery effluent.

Suspended solids include both organic and inorganic materials. The inorganic components include sand, silt, and clay. The organic fraction includes such materials as grease, oil, tar, animal and vegetable fats, various fibers, sawdust, hair, and various materials from sewers. These solids may settle out rapidly and bottom deposits are often a mixture of both organic and inorganic solids. They adversely affect fisheries by covering the bottom of the stream or lake with a blanket of material that destroys the fish-food bottom fauna or the spawning ground of fish. Deposits containing organic materials may deplete bottom oxygen supplies and produce hydrogen sulfide, carbon dioxide, methane, and other noxious gases.

In raw water sources for domestic use, state and regional agencies generally specify that suspended solids in streams shall not be present in sufficient concentration to be objectionable or to interfere with normal treatment processes. Suspended solids in water may interfere with many industrial processes, and cause foaming in boilers, or encrustations on equipment exposed to water, especially as the temperature rises. Suspended solids are undesirable in water for textile industries; paper and pulp; beverages; dairy products; laundries; dyeing; photography; cooling systems, and power plants. Suspended particles also serve as a transport mechanism for pesticides and other substances which are readily adsorbed into or onto clay particles.

Solids may be suspended in water for a time, and then settle to the bed of the stream or lake. These settleable solids discharged with man's wastes may be inert, slowly biodegradable materials, or rapidly decomposable substances. While in suspension, they increase the turbidity of the water, reduce light penetration and impair the photosynthetic activity of aquatic plants.

Solids in suspension are aesthetically displeasing. When they settle to form sludge deposits on the stream or lake bed, they are often much more damaging to the life in water, and they retain the capacity to displease the senses. Solids, when transformed to sludge deposits, may do a variety of damaging things, including blanketing the stream or lake bed and thereby destroying the living spaces for those benthic organisms that would otherwise occupy the habitat. When of an organic and therefore decomposable nature, solids use a portion or all of the dissolved oxygen available in the area. Organic materials also serve as a seemingly inexhaustible food source for sludgeworms and associated organisms.

Typical total suspended solids raw waste concentrations for each subcategory are listed below:

Subcategory	TSS RWL Range, mg/l
Topping	10 - 40
Cracking	10 - 100
Petrochemical	50 - 200
Lube	80 - 300
Integrated	20 - 200

Total suspended solids concentrations for typical raw municipal waste waters range from 100 to 300 mg/l.

Freon Extractables - Oil and Grease

No solvent is known which will directly dissolve only oil or grease, thus the manual "Methods for the Chemical Analysis of Water and Wastes 1971" distributed by the Environmental Protection Agency states that their method for oil and grease determinations includes the freon extractable matter from waters.

In the petroleum refining industry, oils, greases, various other hydrocarbons and some inorganic compounds will be included in the freon extraction procedure. The majority of material removed by the procedure in a refinery waste water will, in most instances, be of a hydrocarbon nature. These hydrocarbons, predominately oil and grease type compounds, will make their presence felt in the COD, TOC, TOD, and usually the BOD tests where high test values will result. The oxygen demand potential of these freon extractables is only one of the detrimental effects exerted on water bodies by this class of compounds. Oil emulsions may adhere to the gills of fish or coat and destroy algae or other plankton. Deposition of oil in the bottom sediments can serve to exhibit normal benthic growths, thus interrupting the aquatic food chain. Soluble and emulsified materials ingested by fish may taint the flavor of the fish flesh. Water soluble components may exert toxic action on fish. The water insoluble hydrocarbons and free floating emulsified oils in a waste water will affect stream ecology by interfering with oxygen transfer, by damaging the plumage and coats of water animals and fowls, and by contributing taste and toxicity problems. The effect of oil spills upon boats and shorelines and their production of oil slicks and iridescence upon the surface of waters is well known. The average freon extractable material recorded by a refinery survey for effluent waters from the refineries ranged from a maximum of 37 mg/l tc a minimum of 4. mg/l.

Grease is defined in "Webster's Third New International Dictionary" as a thick lubricant. The class of refinery products known as greases are usually included in the freon extractable portions of a water analysis. Some thick heavy petroleum products coat the silt and sediment of a stream bottom samples which have been contaminated by oily products over a long period. An infrared scan of such an extract done on bottom sediments from the New York Harbor area compares closely to a typical 90 w automative grease. Such bottom contamination can, of course, exert influence upon the aquatic life of a stream, estuary, bay or other water body. Typical oil and grease concentrations for each subcategory are listed below:

Subcategory	Freon Extractables as Oil and Grease RWL Range, mg/l
Topping	10 - 50
Cracking	15 - 300
Petrochemical	20 - 250
Lube	40 - 400
Integrated	20 - 500

Ammonia as Nitrogen

Ammonia is commonly found in overhead condensates from distillation and cracking and from desalting. It is usually found combined with sulfide as an ammonium sulfide salt. Ammonia is a common product of the decomposition of organic matter. Dead and decaying animals and plants along with human and animal body wastes account for much of the ammonia entering the aquatic ecosystem. Ammonia exists in its non-ionized form only at higher pH levels and is the most toxic in this state. The lower the pH, the more ionized ammonia is formed and its toxicity decreases. Ammonia, in the presence of dissolved oxygen, is converted to nitrate (NO_3) by nitrifying bacteria. Nitrite (NO_2), which is an intermediate product between ammonia and nitrate, sometimes occurs in quantity when depressed oxygen conditions permit. Ammonia can exist in several other chemical combinations including ammonium chloride and other salts.

Nitrates are considered to be among the poisonous ingredients of mineralized waters, with potassium nitrate being more poisonous than sodium nitrate. Excess nitrates cause irritation of the mucous linings of the gastrointestinal tract and the bladder; the symptoms are diarrhea and diuresis, and drinking one liter of water containing 500 mg/l of nitrate can cause such symptoms.

Infant methemoglobinemia, a disease characterized by certain specific blood changes and cyanosis, may be caused by high nitrate concentrations in the water used for preparing feeding formulae. While it is still impossible to state precise concentration limits, it has been widely recommended that water containing more than 10 mg/l of nitrate nitrogen (NO_3-N) should not be used for infants. Nitrates are also harmful in fermentation processes and can cause disagreeable tastes in beer. In most natural water the pH range is such that ammonium ions (NH_4^+) predominate. In alkaline waters, however, high concentrations of un-ionized ammonia in undissociated ammonium hydroxide increase the toxicity of ammonia solutions. In streams polluted with sewage, up to one half of the nitrogen in the sewage may be in the form of free ammonia, and sewage may carry up to 35 mg/l of total nitrogen. It has been shown that at a level of 1.0 mg/l un-ionized ammonia, the ability of hemoglobin to combine with oxygen is impaired and fish may suffocate. Evidence indicates that ammonia exerts a considerable toxic effect on all aquatic life within a range of less than 1.0 mg/l to 25 mg/l, depending on the pH and dissolved oxygen level present.

Ammonia can add to the problem of eutrophication by supplying nitrogen through its breakdown products. Some lakes in warmer climates, and others that are aging quickly are sometimes limited by the nitrogen available. Any increase will speed up the plant growth and decay process.

Typical ammonia as nitrogen raw waste concentrations for each subcategory are listed below:

Subcategory	NH_3 - N RWL Range, mg/l
Topping	0.05 - 20
Cracking	0.5 - 200
Petrochemical	4 - 300
Lube	1 - 120
Integrated	1 - 250

Phenolic Compounds

Catalytic cracking, crude distillation, and product finishing and treating, are the major sources of phenolic compounds. Catalytic cracking produces phenols by the decomposition of multi-cyclicaromatics, such as anthracene and phenanthrene. Some solvent refining processes use phenol as a solvent and although it is salvaged by recovery processes, losses are inevitable.

Many phenolic compounds are more toxic than pure phenol; their toxicity varies with the combinations and general nature of total wastes. The effect of combinations of different phenolic compounds is cumulative.

Phenols and phenolic compounds are both acutely and chronically toxic to fish and other aquatic animals. Also, chlorophenols produce an unpleasant taste in fish flesh that destroys their recreational and commercial value.

It is necessary to limit phenolic compounds in raw water used for drinking water supplies, as conventional treatment methods used by water supply facilities do not remove phenols. The ingestion of concentrated solutions of phenols will result in severe pain, renal irritation, shock and possibly death.

Phenols also reduce the utility of water for certain industrial uses, notably food and beverage processing, where it causes unpleasant tastes and odors in the product.

Typical phenolic raw waste concentrations for each subcategory are listed below:

Subcategory	Phenolics, RWL Range, mg/l
Topping	0-200
Cracking	0-100
Petroleum	0.5-50
Lube	0.1-25
Integrated	0.5-50

Sulfides

In the petroleum refining industry, major sources of sulfide wastes are crude desalting, crude distillation and cracking processes. Sulfides cause corrosion, impair product quality, and shorten the useful catlyst life. They are removed by caustic, diethanciamine, water or steam, or appear as sour condensate waters in these initial processing operations. Hydrotreating processes can be used to remove sulfides in the feedstock. Most removed and recovered sulfide is burned to produce sulfuric acid or elemental sulfur.

When present in water, soluble sulfide salts can reduce pH; react with iron and other metals to cause black precipitates; cause odor problems; and can be toxic to aquatic life. The toxicity of solutions of sulfides to fish increases as the pH value is lowered. Sulfides also chemically react with dissolved oxygen present in water, thereby lowering dissolved oxygen levels.

Typical sulfide raw waste concentrations for each subcategory are listed below:

Subcategory	Sulfide, RWL Range, mg/l
Topping	0-5
Cracking	0-400
Petroleum	0-200
Lube	0-40
Integrated	0-60

Total Chromium

Chromium may exist in water supplies in both the hexavalent and trivalent state. Chromium salts are used extensively in industrial processes and chromate compounds are frequently added to cooling water for corrosion control. The toxicity of chromium salts toward aquatic life varies widely with the species, temperature, pH, concentration, and synergistic or antagonisitc effects of other water constituents, especially hardness.

Chromium, in its various valence states, is hazardous to man. It can produce lung tumors when inhaled and induces skin sensitizations. Large doses of chromates have corrosive effects on the intestinal tract and can cause inflammation of the kidneys. Levels of chromate ions that have no effect on man appear to be so low as to prohibit determination to date.

The toxicity of chromium salts toward aquatic life varies widely with the species, temperature, pH, valence of the chromium, and synergistic or antagonistic effects, especially that of hardness. Fish are relatively tolerant of chromium salts, but fish food organisms and other lower forms of aquatic life are extremely sensitive. Chromium also inhibits the growth of algae.

In some agricultural crops, chromium can cause reduced growth or death of the crop. Adverse effects of low concentrations of chromium on corn, tobacco and sugar beets have been documented.

Typical total chromium raw waste load concentrations for each subcategory are listed below:

Subcategory	Total Chromium, RWL Range, mg/l
Topping	0-3
Cracking	0-6
Petrochemical	0-5
Lube	0-2
Integrated	0-2

Hexavalent Chromium

The hexavalent chromium content of potable water supplies within the U.S. has been reported to vary between 3 to 40 micrograms per liter. In the +6 oxidation state; chromium is usually combined with oxygen in the form of the oxide, chromium trioxide CrO_3 or the Oxyanions chromate $CrO_4^=$ and dichromate Cr_2O_7. Chromates will generally be present in a refinery waste stream when they are used as corrosion inhibitors in cooling water.

Other Pollutants

Other pollutants which were examined in this study of refining waste water practices included: total dissolved solids, cyanide, zinc, temperature, various metallic ions, chloride, fluoride and phosphates.

It was determined that these parameters are generally found in refineries in small enough amounts as not to warrant accross the board treatment. Restrictions on these parameters may be required as a result of water quality requirements.

Zinc

Zinc is an essential and beneficial element in human metabolism when its intake to an organism is limited. At higher amounts zinc can lead to gastrointestinal irritation and large amounts of the metal have been reported to upset trickling filter and activated sludge waste treatment processes.

Concentrations of zinc in excess of 5 mg/1 in raw water used for drinking water supplies cause an undesirable taste which persists through conventional treatment. Zinc can have an adverse effect on man and animals at high concentrations.

In soft water, concentrations of zinc ranging from 0.1 to 1.0 mg/1 have been reported to be lethal to fish. Zinc is thought to exert its toxic action by forming insoluble compounds with the mucous that covers the gills, by damage to the gill epithelium, or possibly by acting as an internal poison. The sensitivity of fish to zinc varies with species, age and condition, as well as with the physical and chemical characteristics of the water. Some acclimatization to the presence of zinc is possible. It has also been observed that the effects of zinc poisoning may not become apparent immediately, so that fish removed from zinc-contaminated to zinc-free water (after 4-6 hours of exposure to zinc) may die 48 hours later. The presence of copper in water may increase the toxicity of zinc to aquatic organisms, but the presence of calcium or hardness may decrease the relative toxicity.

Observed values for the distribution of zinc in ocean waters vary widely. The major concern with zinc compounds in marine waters is not one of acute toxicity, but rather of the long-term sub-lethal effects of the metallic compounds and complexes. From an acute toxicity point of view, invertebrate marine animals seem to be the most sensitive organisms tested. The growth of the sea urchin, for example, has been retarded by as little as 30 ug/l of zinc.

Zinc sulfate has also been found to be lethal to many plants, and it could impair agricultural uses.

Zinc compounds can be used as corrosion inhibitors for cooling water. In addition, zinc is produced in the combustion of fossil fuels and may find its way into refining waters by leaching processes.

A survey of effluents from petroleum refineries across the U.S. reports zinc concentrations of .04 to 1.84 mg/l in the effluent waters. The median concentration of zinc found in the effluents was .16 mg/l.

TDS

Dissolved solids in refinery waste waters consist mainly of carbonates, chlorides, and sulfates. U.S. Public Health Service Drinking Water Standards for total dissolved solids are set at

500 mg/L on the basis of taste thresholds. Many communities in the United States use water containing from 2,000 to 4,000 mg/l of dissolved solids. Such waters are not palatable and may have a laxative effect on certain people. However, the geographic location and availability of potable water will dictate acceptable standards. The following is a summary of a literature survey indicating the levels of dissolved solids which should not interfere with the indicated beneficial use:

Domestic Water Supply	1,000 mg/l
Irrigation	700 mg/l
Livestock Watering	2,500 mg/l
Freshwater Fish and Aquatic Life	2,000 mg/l

Median total dissolved solids concentrations for refinery effluents are 400-700 mg/L. The extensive amount of process water recycle and reuse is primarily responsible for these high concentrations.

Because dissolved solids concentrations are intimately tied to process recycle and the quality of the process raw water source; it is recommended that this parameter be dictated by local water quality requirements.

Cyanides

Cyanides in water derive their toxicity primarily from undissolved hydrogen cyanide (HCN) rather than from the cyanide ion (CN^-). HCN dissociates in water into H^+ and CN^- in a pH-dependent reaction. At a pH of 7 or below, less than 1 percent of the cyanide is present as CN^-; at a pH of 8, 6.7 percent; at a pH of 9, 42 percent; and at a pH of 10, 87 percent of the cyanide is dissociated. The toxicity of cyanides is also increased by increases in temperature and reductions in oxygen tensions. A temperature rise of 10°C produced a two- to threefold increase in the rate of the lethal action of cyanide.

Cyanide has been shown to be poisonous to humans, and amounts over 18 ppm can have adverse effects. A single dose of 6, about 50-60 mg, is reported to be fatal.

Trout and other aquatic organisms are extremely sensitive to cyanide. Amounts as small as .1 part per million can kill them. Certain metals, such as nickel, may complex with cyanide to reduce lethality especially at higher pH values, but zinc and cadmium cyanide complexes are exceedingly toxic.

When fish are poisoned by cyanide, the gills become considerably brighter in color than those of normal fish, owing to the inhibition by cyanide of the oxidase responsible for oxygen transfer from the blood to the tissues.

Cyanide raw waste load data for the refining industry show median values of 0.0 - 0.18 mg/L for the five subcategories. Only occasionally are any values found above 1.0 mg/l. At these concentration ranges, no inhibition is expected in biological waste facilities. Consequently, the values are such that specific limitations are not required. Cyanides are on the EPA toxic materials list and limitations based on health effects will be made available at a later date.

pH (Acidity and Alkalinity)

The acidity of a waste is a measure of the quantity of compounds contained therein which will dissociate in an aqueous solution to produce hydrogen ions. Acidity in petroleum refining waste waters can be contributed by both organic and inorganic compound dissociation. Most mineral acids found in waste waters (sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid) are typically strong acids. The most common weaker acids found include the organic acids such as carboxyl and carbonic.

Compounds which contribute to alkalinity in waste waters are those which dissociate in aqueous solutions to produce hydroxyl ions. Alkalinity is often defined as the acid-consuming ability of the waste water and is measured by titrating a given volume of waste with standard acid until all of the alkaline material has reacted to form salts. In effect, alkalinity is the exact opposite of acidity; high alkalinities lower the hydrogen ion concentration of a solution and raise its pH.

Most refinery waste waters are alkaline due to the presence of ammonia and the use of caustic for sulfur removal. Cracking (both thermal and catalytic) and crude distillation are the principal sources of alkaline discharges. Alkylation and polymerization utilize acids as catalysts and produce severe acidity problems.

Extreme pH values are to be avoided because of effects on emulsification of oil, corrosion, precipitation, volatilization of sulfides and other gases, etc. In streams and water courses, extreme pH levels accentuates the adverse effects of other pollutants as well as causing toxicity itself.

The hydrogen ion concentration in an aqueous solution is represented by the pH of that solution. The pH is defined as the negative logarithm of the hydrogen ion concentration in a solution. The pH scale ranges from zero to fourteen, with a pH of seven, representing neutral conditions, i.e., equal concentrations of hydrogen and hydroxyl ions. Values of pH less than seven indicate increasing hydrogen ion concentration or acidity; pH values greater than seven indicate increasing alkaline conditions. The pH value is an effective parameter for predicting chemical and biological properties of aqueous solutions. It should be emphasized that pH cannot be used to predict the quantities of alkaline or acidic materials in a water sample. However, most effluent and stream standards are based on maximum and minimum allowable pH values rather than on alkalinity and acidity.

Since pH RWL values are not additive, it is not always possible to predict the final pH of a process waste water made up of multiple discharges. In addition, the individual refinery's discharge characteristics will dictate final pH ranges, which may be kept within the acceptable range merely by equalization, or which may require more sophisticated neutralization facilities. However, it is recommended that a pH range of 6.0 to 9.0 be established as the effluent limitation.

Temperature

Crude desalting, distillation, and cracking contribute substantial thermal wasteloads.

Temperature is one of the most important and influential water quality characteristics. Temperature determines those species that may be present; it activates the hatching of young, regulates their activity, and stimulates or suppresses their growth and development; it attracts, and may kill when the water becomes too hot or becomes chilled too suddenly. Colder water generally suppresses development. Warmer water generally accelerates activity and may be a primary cause of aquatic plant nuisances when other environmental factors are suitable.

Temperature is a prime regulator of natural processes within the water environment. It governs physiological functions in organisms and, acting directly or indirectly in combination with other water quality constituents, it affects aquatic life with each change. These effects include chemical reaction rates, enzymatic functions, molecular movements, and molecular exchanges between membranes within and between the physiological systems and the organs of an animal.

Chemical reaction rates vary with temperature and generally increase as the temperature is increased. The solubility of gases in water varies with temperature. Dissolved oxygen is decreased by the decay or decomposition of dissolved organic substances and the decay rate increases as the temperature of the water increases reaching a maximum at about 30°C (86°F). The temperature of stream water, even during summer, is below the optimum for pollution-associated bacteria. Increasing the water temperature increases the bacterial multiplication rate when the environment is favorable and the food supply is abundant.

Reproduction cycles may be changed significantly by increased temperature because this function takes place under restricted temperature ranges. Spawning may not occur at all because temperatures are too high. Thus, a fish population may exist in a heated area only by continued immigration. Disregarding the decreased reproductive potential, water temperatures need not reach lethal levels to decimate a species. Temperatures that favor competitors, predators, parasites, and disease can destroy a species at levels far below those that are lethal.

Fish food organisms are altered severely when temperatures approach or exceed 90°F. Predominant algal species change, primary production is decreased, and bottom associated organisms may be depleted or altered drastically in numbers and distribution. Increased water temperatures may cause aquatic plant nuisances when other environmental factors are favorable.

Synergistic actions of pollutants are more severe at higher water temperatures. Given amounts of domestic sewage, refinery wastes, oils, tars, insecticides, detergents, and fertilizers more rapidly deplete oxygen in water at higher temperatures, and the respective toxicities are likewise increased.

When water temperatures increase, the predominant algal species may change from diatoms to green algae, and finally at high temperatures to blue-green algae, because of species temperature preferentials. Blue-green algae can cause serious odor problems. The number and distribution of benthic organisms decreases as water temperatures increase above 90°F, which is close to the tolerance limit for the population. This could seriously affect certain fish that depend on benthic organisms as a food source.

The cost of fish being attracted to heated water in winter months may be considerable, due to fish mortalities that may result when the fish return to the cooler water.

Rising temperatures stimulate the decomposition of sludge, formation of sludge gas, multiplication of saprophytic bacteria and fungi (particularly in the presence of organic wastes), and the consumption of oxygen by putrefactive processes, thus affecting the esthetic value of a water course.

In general, marine water temperatures do not change as rapidly or range as widely as those of freshwaters. Marine and estuarine fishes, therefore, are less tolerant of temperature variation. Although this limited tolerance is greater in estuarine than in open water marine species, temperature changes are more important to those fishes in estuaries and bays than to those in open marine areas, because of the nursery and replenishment functions of the estuary that can be adversely affected by extreme temperature changes.

Other Metallic Ions

Several metallic ions in addition to chormium and zinc may be found in refinery effluents. The major sources for their presence in waste water are from the crude itself and corrosion products. The concentration of metallic ions varies considerably dependent upon the effectiveness of catalyst recovery in production process. Table 25 lists those metals which may be commonly found in petroleum refinery effluents. Dissolved metallic ions create turbidity and discoloration, can precipitate to form bottom sludges, and can impart taste to water.

TABLE 25

Metallic Ions Commonly Found in Effluents from Petroleum Refineries

Aluminum
Arsenic
Cadmium
Chromium
Cobalt
Copper
Iron
Lead
Mercury
Nichel
Vanadium
Zinc

Metallic ions such as copper, and cadmium are toxic to microorganisms because of their ability to tie up the proteins in the key enzyme systems of the microogranisms.

Chlorides:

Chloride ion is one of the major anions found in water and produces a salty taste at a concentration of about 250 mg/l. Concentrtations of 1000 mg/l may be undetectable in waters which contain appreciable amounts of calcium and magnesium ions.

Water is invariably associated with naturally occurring hydrocarbons underground and much of this water contains high amounts of sodium chloride. The saltiest oil field waters are located in the mid-continent region of the country where the average dissolved solids content is 174,000 ppm; therefore, waters containing high levels of salt may be expected.

Copper chloride may be used in a sweetening process and aluminum chloride in catalytic isomerization. These products may also find their ways to waste streams.

The toxicity of chloride salts will depend upon the metal with which they are combined. Because of the rather high concentration of the anion necessary to initiate detrimental biological effects, the limit set upon the concentration of the metallic ion with which it may be tied, will automatically govern its concentration in effluents, in practically all forms except potassium, calcium, mganesium, and sodium.

Since sodium is by far the most common (sodium 75 percent, magnesium 15 percent, and calcium 10 percent) the concentration of this salt will probably govern the amount of chlorides in waste streams from petroleum refineries.

It is extremely difficult to pinpoint the exact amount of sodium chloride salt necessary to result in toxicity in waters. Large concentrations have been proven toxic to sheep, swine, cattle or poultry.

In swine fed diets of swill containing 1.5 to 2.0% salt by weight, poisoning symptoms can be induced if water intake is limited and other factors are met. The time interval necessary to accomplish this is still about one full day of feeding at this level.

Since problems of corrosion, taste and quality of water necessary for industrial or agricultural purposes occur at sodium chloride concentration levels below those at which toxic effects are experienced, these factors will undoubtedly determine the amount of chlorides allowed to escape in waste streams from refining operations. The study of refinery effluents previously mentioned, placed net chloride levels at values ranging from 57 to 712 mg/l. The median value was 176 mg/l.

Fluoride: HF

Alkalation units (when hydrofluoric acid is used) can contribute fluoride ion to the plant's waste effluent. Since calcium and barium fluoride are insoluble in water the fluorides will by necessity be associated with other cations.

In concentrations of approximately 1 mg/l in potable water supplies fluorides have been found to be an effective preventor of dental cavities. In concentrations greater than this amount, fluorides can cause molting of tooth enamel and may be incorporated into the bones.

Natural waters can contain levels of fluorides up to 10 ppm. If these waters are to be used for potable supplies or for certain industrial or agricultural purposes the fluoride levels must be reduced. Since many municipal waters are artificially fluoridated as a dental health aid, the U.S. Public Health Service has placed limits on the total amounts of fluorides a water supply may contain. Their recommended control levels depend upon temperature and are expressed as lower, optimum, and upper limits. Optimum limits range from .7 to 1.2 mg/l. If values exceed two times the optimum value, the supply must be rejected or the fluoride content lowered. Because refinery effluents may empty into water ways which may eventually become public supplies, the maximum permissible limits of fluorides present in an effluent will probably be derived from the USPHS control limits for drinking water.

Phosphate - Total

Various forms of phosphates find their way into refinery effluents. They range through several organic and inorganic species and are usually contributed by corrosion control chemicals. Plant cooling systems may contain 20 to 50 mg/l of phosphate ion.

Phosphorus is an element which is essential to growth of an organism. It may at times become a growth limiting nutrient in the biological system of a water body. In these instances an over abundance of the element contributed from an outside source may stimulate the growth of photosynthetic aquatic macro and micro-organisms resulting in nuisance problems. Since the forms of phosphorus in waters or industrial wastes are so varied, the term total phosphate has been used to indicate all the phosphate present in an analyzed sample regardless of the chemical form. Also, many phosphorus compounds tend to degrade rather readily, and in these less complex forms phosphate may be readily utilized in the aquatic life cycle. It is therefore reasonable to direct concern toward the total amount of phosphorus present rather than chemical structure it may assume, for in only very unusual cases may the form or concentration of the element present in a waste stream be toxic. Total phosphate values noted on a nationwide refinery survey were 9.49 mg/l maximum and .096 mg/l minimum for effluents. The median value was .68 mg/l expressed as phosphorus.

SECTION VII

CONTROL AND TREATMENT TECHNOLOGY

Petroleum refinery waste waters vary in quantity and quality from refinery to refinery. However, the wastes are readily treatable. The results of the industry survey indicate, as would be expected, that techniques for in-process control are general across the industry and the specific application of these techniques at individual plants determines their success. Local factors such as climate, discharge criteria, availability of land, or other considerations may dictate the use of different waste water treatment processes to reach an acceptable effluent. The survey has shown that although the end-of-pipe waste water treatment technologies used throughout the petroleum refining industry have a marked similarity in operational steps, a considerable variation in treatment results exist. The processes used for treating refinery waste water, however, are similar in purpose; namely--maximizing oil recovery and minimizing the discharge of other pollutants. The wastewater treatment technology described below is generally applicable across all industry subcategories.

In-Plant Control/Treatment Techniques

In-plant practices are the sole determinant of the amount of waste water to be treated. There are two types of in-plant practices that reduce flow to the treatment plant. First, reuse practices involving the use of water from one process in another process. Examples of this are: using stripper bottoms for makeup to crude desalters; using blowdown from high pressure boilers as feed to low pressure boilers; and using treated effluent as makeup water whereever possible. Second, recycle systems that use water more than once for the same purpose. Examples of recycle systems are: the use of steam condensate as boiler feedwater; and cooling towers. The reduction or elimination of a waste stream allows the end-of-pipe processes to be smaller, provide better treatment, and be less expensive. Since no treatment process can achieve 100 percent pollutant removal from the individual stream, reduction in flow allows for a smaller pollutant discharge.

Housekeeping

In addition to reuse/recycle of water streams and reduction in flows by other in-plant techniques, another effective in-plant control is good housekeeping. Examples of good housekeeping practices are: minimizing waste when sampling product lines; using vacuum trucks or dry cleaning methods to clean up any oil spills; using a good maintenance program to keep the refinery as leakproof as possible; and individually treating waste streams with special characteristics, such as spent cleaning solutions.

The use of dry cleaning, without chemicals, aids in reducing water discharges to the sewer. Using vacuum trucks to clean up spills and charging of this recovered material to slop oil tanks, reduces the discharge of both oil and water to the waste water system. The oil can also be recovered for reprocessing. Process units should be curbed to prevent the contamination of clean areas with oily storm runoff and to prevent spills from spreading widely. Prompt cleanup of spills will also aid in reducing discharges to the sewer systems. Additionally, sewers should be flushed regularly to prevent the buildup of material in the sewer, eliminating sudden surges of pollutants during heavy rains. Collection vessels should also be provided whenever maintenance is performed on liquid processing units, to prevent accidental discharges to the sewers.

Operations during turnaround present special problems. Wastes generated by cleaning tanks and equipment should be collected, rather than draining directly to the sewer. The wastes from these holding tanks should be gradually bled to the sewer, after first pretreating as necessary to eliminate deleterious effects on the waste water treatment system. An alternative method of disposal is through the use of contract carriers.

While these are not all the examples of good housekeeping practices which can be cited for refinery operations, it is evident that housekeeping practices within a refinery can have substantial impact on the loads discharge to the waste treatment facilities. The application of good housekeeping practices to reduce waste loads requires judicious planning, organization and operational philosophy.

Process Technology

Many of the newer petroleum refining processes are being designed or modified with reduction of water use and subsequent minimization of contamination as design criteria; although no major innovations in basic refining technology are anticipated. Improvements which can be expected to be implemented in existing refineries are: primarily dedicated to better control of refinery processes and other operations; elimination of marginal processing operations, and specific substitution of processes and/or cooling techniques to reduce discharge loads to waste treatment facilities. Examples of the possible changes which may be implemented include:

1. Substitution of improved catalysts which have higher activity and longer life, consequently requiring less regeneration and resulting in lower waste water loads.

2. Replacement of barometric condensers with surface condensers or air fan coolers, reducing a major oil-water emulsion source. As an alternative, several refineries are using oily water cooling tower systems, with the barometric condensers, equipped with oil separation/emulsion breaking auxiliary equipment.

3. Substitution of air fan coolers to relieve water cooling duties simultaneously reduces blowdown discharges.

4. Installation of hydrocracking and hydrotreating processes will allow generation of lower waste loadings than the units they replace. The rapid pace at which such units are being installed is exerting and will continue to exert a strong influence on the reduction of waste loadings, particularly sulfides and spent caustics.

5. Installation of automatic monitoring instrumentation, such as TOC monitors, will allow early detection of process upsets which result in excessive discharges to sewers.

6. Increased use of improved drying, sweetening, and finishing procedures will minimize spent caustics and acids, water washes, and filter solids requiring disposal.

Cooling Towers

Cooling towers eliminate large volumes of once through cooling water by passing heated water through heat exchange equipment. By recycling the cooling water many times, the amount of water used is greatly reduced. The number of times cooling water can be reused is determined by the total dissolved solids (TDS) content of the water, and the effects high dissolved solids have on process equipment. When the TDS becomes too high, scaling occurs and heat transfer efficiency decreases. The TDS level in the circulating water is controlled by discharging a portion of the steam (blowdown) from the system. The higher the allowable TDS level, the greater number of cycles of concentration and the less make-up water is required (87). Installation of cooling towers will reduce the amount of water used within the refinery by at least 90 percent (87).

There are three types of cooling towers (106); wet or evaporative, dry, and combined "wet-dry."

Evaporative Cooling Systems

Evaporative cooling systems transport heat by transfer of the latent heat of vaporization. This results in a temperature decrease of circulating water and a temperature and humidity increase of cooling air.

Spray ponds are an evaporative cooling system using natural air currents and forced water movement. Because of their inefficiency, spray ponds are used less in industry than cooling towers. Cooling towers have a higher efficiency because they provide more intimate contact between the air and water. As the water falls over the packing, it exposes a large contact surface area. As the water heats up the air, the air can absorb more water. The more water evaporated, the more heat is transferred (106). Because an evaporative cooling tower is dependent on ambient temperatures and humidity, its performance is variable throughout the year. There are three types of evaporative cooling towers: mechanical draft towers; atmospheric towers, which use wind or natural air currents; and natural draft towers, which use tall stacks to move air by stack effect. Most refineries use mechanical draft towers, which have baffles, called drift eliminators, to separate entrained water from the air stream, thus reducing the amount of water carried into the air. The evaporative system is the least costly of all cooling towers.

Dry Cooling Systems

There are two types of dry air cooling systems. Either system can be used with either mechanical or natural draft cooling towers. Most refineries use mechanical draft towers on indirect condensing systems. The tubes used in dry cooling equipment have circumferential fins to increase the heat transfer area. Most tube designs have an outside to inside surface area ratio of 20:1. (106) The advantage of the dry air system is that it requires no makeup water and there is no water entrainment. Dry air cooling systems are being increasingly used to reduce the amount of water discharged to the waste water treatment plant. A disadvantage of the dry cooling process is that it has low rates of heat transfer requiring large amounts of land and uses more power than other cooling systems. The dry cooling tower is also more expensive to install than evaporative systems.

Wet-Dry Systems

The wet-dry systems use an evaporative and non-evaporative cooling tower in either series or parallel, each of which can be operated with a mechanical or natural draft tower. The series design has the evaporative cooling process preceeding the dry process with respect to the air flow. This lowers the temperature of the air entering the dry process which would mean a smaller unit could be used. The problem with this method is that solids are deposited in the dry tower due to drift from the wet section. The parallel process uses a dry cooling tower upstream of the wet section, each of which has its own air supply. The two air streams are mixed and discharged, reducing the vapor plume.

Recycle/Reuse Practices

Recycle/reuse can be accomplished either by return of the waste water to its original use, or by using it to satisfy a lower quality demand. The recycle/reuse practices within the refining industry are extremely varied and only a few examples are described briefly below:

1. Reduction of once-through cooling water results in tremendously decreased total effluents.

2. Sour water stripper bottoms are being used in several refineries as make-up water for crude desalter operations. These sour water bottoms are initially recovered from overhead accumulators on the catalytic cracking units.

3. Regeneration of contact process steam from contaminated condensate will reduce the contact process waste water to a small amount of blowdown. This scheme can be used to regenerate steam in distillation towers or dilution steam stripping in pyrolysis furnaces.

4. Reuse of waste water treatment plant effluent as cooling water, as scrubber water, or as plant make-up water, reduces total make-up requirements.

5. Cooling tower blowdowns are frequently reused as seal water on high temperature pump service, where mechanical seals are not practicable.

6. Storm water retention ponds are frequently used as a source of fire water or other low quality service waters.

Many other conservation methods can be implemented, such as the use of stripped sour water as low pressure (LP) boiler make-up, and LP boiler blowdown as make-up water for crude desalting. However, these, and the other possible recycle/reuse cases outlined above must be examined by the individual refinery in light of its possible advantages/disadvantages, insofar as product quality or refining process capabilities are affected. For example, one refinery has reported that reuse of sour water stripper bottoms for desalting resulted in a desalted crude which was difficult to process downstream.

At-Source Pretreatment

Major at-source pretreatment processes which are applicable to individual process effluents or groups of effluents within a refinery are stripping of sour waters, neutralization and oxidation of spent caustics, ballast water separation, and slop oil recovery. The particular areas of application of these processes are discussed below.

Sour Water Stripping

Sour or acid waters are produced in a refinery when steam is used as a stripping medium in the various cracking processes. The hydrogen sulfide, ammonia and phenols distribute themselves between the water and hydrocarbon phases in the condensate. The concentrations of these pollutants in the water vary widely depending on crude sources and processing involved.

The purpose of the treatment of sour water is to remove sulfides (as hydrogen sulfide, ammonium sulfide, and polysulfides) before the waste enters the sewer. The sour water can be treated by: stripping with steam or flue gas; air oxidation to convert hydrogen sulfide to thiosulfates; or vaporization and incineration.

Sour water strippers are designed primarily for the removal of sulfides and can be expected to achieve 85-99 percent removal. If acid is not required to enhance sulfide stripping, ammonia will also be stripped with the percentage varying widely with stripping temperature and pH. If acid is added to the waste water, essentially none of the ammonia will be removed. Thus, ammonia removals in sour water strippers vary from 0 to 99 percent. Depending upon such conditions as waste water pH, temperature, and contaminant partial pressure; phenols and cyanides can also be stripped with removal as high as 30 percent. The bottoms from the stripper usually go to the desalter where most of the phenols are extracted and the waste water can be sent to the regular process water treating plant. COD and BOD_5 are reduced because of the stripping out of phenol and oxidizable sulfur compounds.

The heated sour water is stripped with steam or flue gas in a single stage packed or plate-type column. Two-stage units are also being installed to enhance the separate recovery of sulfide streams and ammonia streams. Hydrogen sulfide released from the waste water can be recovered as sulfuric acid or sulfur, or may be burned in a furnace. The bottoms have a low enough sulfide concentration to permit discharge into the general waste water system for biological treatment. If the waste contains ammonia, it is neutralized with acid before steam stripping. The waste liquid passes down the stripping column while the stripping gas passes upward. Most refiners now incinerate th sour water stripper acid gases without refluxing the stripper. This converts the ammonia to nitrogen with possibly traces of nitrogen oxides. Due to the high concentrations of sulfur dioxide produced more complex processing will probably be required in the future.

Several stripping processes are available. These include: Chevron WWT; ammonium sulfate production; a dual burner Claus sulfur plant; and the Howe-Baker ammonex process. Deep well injection and oxidation to the thiosulfate are also being used, but in the future probably won't do a good enough job.

The Chevron WWT process (37) is basically two stage stripping with ammonia pruification, so that the hydrogen sulfide and ammonia are separated. The hydrogen sulfide would go to a conventional Claus sulfur plant and the ammonia can be used as fertilizer.

Ammonium sulfate can be produced by treating with sulfuric acid but a very dilute solution is produced and concentrating it for sale as fertilizer is expensive. Again the hydrogen sulfide goes to a conventional Claus sulfur plant.

A dual burner Claus sulfur process is generally the answer in new plants, but adding the second burner to an existing sulfur plant is difficult. The second burner is required to handle the ammonia. A refluxed stripper is required to reduce the water vapor in the hydrogen sulfide-ammonia mixture and the line between the stripper and the Claus Unit must be kept at about 150°F to prevent precipitation of ammonium sulfide complexes.

Howe-Baker Engineers Inc. of Tyler, Texas have developed to the pilot plant stage a process they call "Ammonex". It is a solvent extraction process that basically is intended to complete with the Chevron WWT process. No commercial units have been built.

Another way of treating sour water is to oxidize by aeration. Compressed air is injected into the waste followed by sufficient steam to raise the reaction temperature to at least 190°F. Reaction pressure of 50-100 psig is required. Oxidation proceeds rapidly and converts practically all the sulfides to thiosulfates and about 10 percent of the thiosulfates to sulfates. Air oxidation, however, is much less effective than stripping in regard to reduction of the oxygen demand of sour waters, since the remaining thiosulfates can later be oxidized to sulfates by aquatic microorganisms.

The stripping of sour water is normally carried out to remove sulfides and hence, the effluent may contain 50-100 ppm of ammonia, or even considerably higher, depending on the influent ammonia concentration. Values of ammonia have been reported as low as 1 ppm, but generally the effluent ammonia concentration is held to approximately 50 ppm to provide nutrient nitrogen for the refinery biological waste treatment system (2,14,33,58).

Spent Caustic Treatment

Caustic solutions are widely used in refining. Typical uses are to neutralize and extract:

a. Acidic materials that may occur naturally in crude oil.
b. Acidic reaction products that may be produced by various chemical treating processes.
c. Acidic materials formed during thermal and catalytic cracking such as hydrogen sulfide, phenolics, and organic acids.

Spent caustic solutions may therefore contain sulfides, mercaptides sulfates, sulfonates, phenolates, naphthenates, and other similar organic and inorganic compounds.

At least four companies process these spent caustics to market the phenolics and the sodium hyposulfide. However, the market is limited and most of the spent caustics are very dilute so the cost of shipping the water makes this operation uneconomical.

Some refiners neutralize the caustic with spent sulfuric from other refining processes, and charge it to the sour water stripper. This removes the hydrogen sulfide. The bottoms from the sour water stripper go to the desalter where the phenolics are extracted by the crude oil.

Spent caustics usually originate as batch dumps, and the batches may be combined and equalized before being treated and/or discharged to the general refinery waste waters. Spent caustic solutions can also be treated by neutralization with flue gas. In the treatment of spent caustic solutions by flue gas, hydroxides are converted to carbonates. Sulfides, mercaptides, phenolates, and other basic salts are converted by the flue gas stripping. Phenols can be removed and used as a fuel or can be sold. Hydrogen sulfide and mercaptans are usually stripped and burned in a heater. Some sulfur is recovered from stripper gases. The treated solution will contain mixtures of carbonates, sulfates, sulfites, thiosulfates and some phenolic compounds. Reaction time of 16-24 hours is required for the neutralization of caustic solution with flue gas.

The oxidation phase of spent caustic treatment is aimed at the sulfide content of these wastes and achieves 85-99 percent sulfide removal. In this process, sulfides are oxidized primarily to thiosulfates although in some variations there is partial oxidation of the sulfur compounds to sulfate. Oxidation processes are not applied to phenolic caustics, as phenols inhibit oxidation. It should be noted that those processes which oxidize the sulfide only to thiosulfate, satisfy half of the oxygen demand of the sulfur, as thiosulfate can be oxidized biologically to sulfate. Neutralization of spent caustics is applied to both phenolic and sulfidic caustic streams; the sulfidic caustics are also steam stripped, after neutralization, to remove the sulfides. When phenolic spent caustics are neutralized, crude acid oils or "crude carbolates" are sprung and thus removed from the waste water. The major part of the phenols will appear in the oil fraction, but a significant part may remain in the waste water as phenolates.

Fluid bed incineration is also now being used. This process was developed under an EPA demonstration grant (26) and at least two large units are under construction. Once the incinerator is started up, the sludge should provide the necessary heating value to keep the system operating. Oxidizing fuels may be required when the sludge is burnt, as ash remains in the bed of the incinerator. A constant bed level is maintained, so the sand bed originally in the incinerator is gradually replaced by the inert sludge ash (5). The gasses pass through a scrubber, so the fines and particulate matter can be recovered. The ash and fines can be landfilled. This landfill is cleaner than a sludge landfill, because there are no organic materials present to contaminate ground water or run-off.

In the past ocean dumping, deep well injection, evaporative lagoons, and simple dilution have all been used. These methods will no longer be acceptable.

Sewer System Segregation

Waste water quantity is one of the major factors that affect the cost of waste treatment facilities most directly. Water usage in the petroleum refining industry varies from less than 5 gallons of water per barrel of crude charge in the newer refineries to higher than 1000 gallons of water per barrel of crude charge in the older refineries. In order to provide efficient treatment to the wastes originating within a refinery, it is very important that segregation of concentrated waste streams be considered. Segregation of waste streams frequently simplifies waste treating problems as well as reduces treatment facility costs. Thus, treatment of highly polluted waste streams at the source can prevent gross pollution of large volumes of relatively clean waste water. Such treatment is often a more economical solution of a problem than would be possible if wastes are discharged directly to the refinery sewers. Treatment at the source is also helpful in recovering by-products from the wastes which otherwise could not be economically recovered when the wastes are combined.

In areas where water supply is limited, reduced water requirements have been incorporated into the design and operation, thereby reducing total water usage.

To minimize the size of the waste water treatment processes it is imperative polluted water only be treated. This can be guaranteed by segregating the various sewer systems. There should be a sewer carrying process and blowdown waters that are treated continuously. A polluted storm water sewer should go to a storage area from which it can be gradually discharged to the treatment facilities. A sewer system containing clean storm water can be discharged directly to the receiving water. The sanitary system should be treated separately from the process water because of the bacteria present in this stream. Once through cooling water should be kept separate because of the large volumes of water involved and the low waste loadings encountered. A connection to the treatment plant should be provided in case of oil leaks into the system.

Storm Water Runoff

An additional source of pollution from a petroleum refinery area is caused by rainfall runoff. Size and age of refinery site, housekeeping, drainage areas, and frequency and intensity of rainfall are several of the factors which compound the assignment of allowable pollutional values.

There are several measures that refiners can provide to minimize storm water loads to their treatment system after diverting all extraneous drainage around the refinery area. The major consideration is a separate storm water sewer and holding system.

By providing separate collection facilities for storm water runoff, protection is afforded the operation of the separator and ancillary treatment systems by controlling the hydraulic load to be treated. Comingling of inorganic particles with oily waste water often times produces an emulsion which is difficult to break in the oil-water separator.

Design of this facility should be based on the maximum ten-year, twenty-four-hour rainfall runoff of the refinery drainage area. Diversion of the collected storm water runoff to the oil-water separator facilities can be provided when hydraulic flows return to normal operations. In the event of excessive collection due to a high intensity storm, diversion facilities should be provided to allow for emergency bypass capability to divert the trailing edge of the runoff hydrograph (the leading edge normally contained the mass of pollutants in urban runoff investigations). An oil retention baffle and an API type overflow weir should be provided to prevent the discharge of free and floating oil.

An alternate to the separate sewer system would be the provision of a storm surge pond that would receive the polluted waters when the flow to the oil-water separator exceeded 15 percent of the normal hydraulic flow. During normal periods, the collected storm water-refinery water could then be diverted to the oil-water separator (provided process flow did not equal or exceed the units hydraulic capacity).

The major cause of pollution by storm water runoff is the lack of housekeeping within the refinery confine. Proper procedures should be encouraged to prevent the accumulation of materials which contribute to pollution due to rainfall runoff. Some of the more common preventive measures are: (1) Provide curbing around process unit pads; (2) Prevent product sample drainage to sewers; (3) Repair pumps and pipes to prevent oily losses to the surface areas; (4) Contain spilled oil from turnarounds; (5) Dike crude and product tank areas and valve precipitation to the storm water sewer.

In the event the collected water needs to be released from the storm water detention pond due to overflow, samples of the water should be monitored for; (1) Oil and Grease, (2) Organic analysis such as TOC.

Ballast Water Separation

Ballast water normally is not discharged directly to the refinery sewer system because the intermittent high-volume discharges. The potentially high oil concentrations, would upset the refinery waste water treatment facilities. Ballast waters may also be treated separately, with heating, settling, and at times filtration as the major steps. The settling tank can also be provided with a steam coil for heating the tank contents to help break emulsions, and an air coil to provide agitation. The recovered oil, which may be considerable, is generally sent to the slop oil system.

Slop Oil Treatment

Separator skimmings, which are generally referred to as slop oil, require treatment before they can be reused, because they contain an excess amount of solids and water. Solids and water contents in excess of about 1 percent generally interfere with processing.

In most cases slop oils are easily treated by heating to 190°F for 12 to 14 hours. At the end of settling, three definite layers exist: a top layer of clean oil; a middle layer of secondary emulsion; and a bottom layer of water containing soluble components, suspended solids, and oil. In some cases, it is advantageous or even necessary to use acid or specific chemical demulsifiers to break slop oil emulsions. The water layer resulting from acid and heat treatment has high BOD and COD, but also low pH, and must be treated before it can be discharged.

Slop oil can also be successfully treated by centrifugation or by precoat filtration using diatomaceous earth as the precoat.

Gravity Separation of Oil

Gravity separators remove a majority of the free oil found in refinery waste waters. Because of the large amounts of reprocessable oils which can be recovered in the gravity separators, these units must be considered an integral part of the refinery processing operation and not a waste water treatment process. The functioning of gravity-type separators depends upon the difference in specific gravity of oil and water. The gravity-type separator will not separate substances in solution, nor will it break emulsions. The effectiveness of a separator depends upon the temperature of the water, the density and size of the oil globules, and the amounts of characteristics of the suspended matter present in the waste water. The "susceptibility to separation" (STS) test is normally used as a guide to determine what portion of the influent to a separator is amenable to gravity separation.

The API separator is the most widely used gravity separator. The basic design is a long rectangular basin, with enough detention time for most of the oil to float to the surface and be removed. Most API separators are divided into more than one bay to maintain laminar flow within the separator, making the separator more effective. API separators are usually equipped with scrapers to move the oil to the downstream end of the separator where the oil is collected in a slotted pipe or on a drum. On their return to the upstream end, the scrapers travel along the bottom moving the solids to a collection trough. Any sludge which settles can be dewatered and either incinerated or disposed of as landfill.

The gravity separator usually consists of a pre-separator (grit chamber) and a main separator, usually rectangular in shape, provided with influent and effluent flow distribution and stilling devices and with oil skimming and sludge collection equipment. It is essential that the velocity distribution of the approach flow be as uniform as possible before reaching the inlet distribution baffle.

Another type of separator finding increasing employment in refineries is the parallel plate separator. The separator chamber is subdivided by parallel plates set at a 45° angle, less than 6 inches apart. This increases the collection area while decreasing the overall size of the unit. As the water flows through the separator the oil droplets coalesce on the underside of the plates and travel upwards where the oil is collected. The parallel plate separator can be used as the primary gravity separator, or following an API separator.

Further Removal of Oil and Solids

If the effluent from the gravity separators is not of sufficient quality to insure effective treatment before entering the biological or physical-chemical treatment system, it must undergo another process to remove oils and solids. Most refineries use either clarifiers, dissolved air flotation units or filters to reduce the oil and solids concentration. Each of these processes has also been used to treat the effluent from a biological system.

Clarifiers

Clarifiers use gravitational sedimentation to remove oil and solids from a waste water stream. Often it is necessary to use chemical coagulants such as alum or lime to aid the sedimentation process. These clarifiers are usually equipped with a skimmer to remove any floating oil. Clarifiers used after a biological system normally do not have skimmers as there should be no floating oils at that point. The sludge from the clarifiers is usually treated before final disposal.

End-of-Pipe Control Technology

End-of-pipe control technology in the petroleum refining industry relies heavily upon the use of biological treatment methods. These are supplemented by appropriate pretreatment to insure that proper conditions, especially sufficient oil removal and pH adjustment, are present in the feed to the biological system. When used, initial treatment most often consists of neutralization for control of pH or equalization basins to minimize shock loads on the biological systems. The incorporation of solids removal ahead of biological treatment is not as important as it is in treating municipal waste waters.

One of the initial criteria used to screen refineries for the field survey, was degree of treatment provided by their waste water treatment facilities. Therefore, the selection of plants was not based on a cross-section of the entire industry, but rather was biased in favor of those segments of the industry that had the more efficient waste water treatment facilities. Table 26 indicates the types of treatment technology and performance characteristics which were observed during the survey. In most of the plants analyzed, some type of biological treatment was utilized to remove dissolved organic material. Table 27 summarizes the expected effluents from waste water treatment processes throughout the petroleum refining industry. Typical efficiencies for these processes are shown in Table 28.

During the survey program, waste water treatment plant performance history was obtained when possible. This historical data were analyzed statistically and the individual plant's performance evaluated in comparison to the original design basis. After this evaluation, a group of plants was selected as being exemplary and these plants were presented in Table 26. The treatment data in Table 28 represent the annual daily average performance (50 percent probability-of-occurrence).

There were enough plants involving only one subcategory to make the interpretation meaningful. In preparing the economic data base, however, all the waste water treatment plant data were analyzed to develop a basis for subsequent capital and operating costs.

The treatment data from the exemplary plants referred to previoulsy were analyzed to formulate the basis for developing BPCTCA effluent criteria. The effluent limitations were based on both these treatment data, other data included in Supplement B, and other sources as discussed in Section IX. These effluent limitations were developed for each subcategory individually and thus no common treatment efficiency was selected as being typical of the petroleum refining industry for use in the BPCTCA effluent limitations. A brief description of the various elements of end-of-pipe treatment follows.

Equalization

The purpose of equalization is to dampen out surges in flows and loadings. This is especially necessary for a biological treatment plant, as high concentrations of certain materials will upset or completely kill the bacteria in the treatment plant. By evening out the loading on a treatment plant, the equalization step enables the treatment plant to operate more effectively and with fewer maintenance problems. Where equalization is not present, an accident or spill within the refinery can greatly affect the effluent quality or kill the biomass (R7, R20).

The equalization step usually consists of a large pond that may contain mixers to provide better mixing of the wastes. In some refineries the equalization is done in a tank (55, R29). The equalization step can be before or after the gravity separator but is more effective before as it increases the overall efficiency of the separator. However, care must be taken to prevent anaerobic decomposition in the equalization facilities.

Observed Refinery Treatment System and Effluent Loadings

TABLE 26

SUBCATEGORY	A	B	B	B	B	B	C	C	C	D	D	E
Type of Treatment	OP	AL-PP	AL-F	E-DAF-AS	OP	DAF,AL,PP	DAF,AS	DAF,AS	DAF,AL,PP	E,TF,AS	E,AS	DAF,AS,PP
Refinery	R32	R18		R27	R26	R7	R20	R8	R23	R24	R28	R25
Observed Average Effluent Loadings Net-kg/1000 m3 of feedstock (lb/1000 bbl of feedstock)												
BOD5		8(2.8)	8.0(4.4)	5.9(2.1)	10(3.6)	3.7(1.3)	13(4.6)	2.7(0.95)	2.6(0.91)	7.4(2.6)	14(5.0)	17.5(6.2)
COD	------	39(13.8)	68(24)	96(34)	71(25.0)	39(13.8)	67(23.5)	------	54(19,	57(20)	136(48)	320(113)
TSS	------	------	25(8.7)	34(12)	8.5(3.0)	4.2(1.5)	13.6(4.8)	8.5(3.0)	7(2.5)	12(4.3)	38(13.5)	36(12.7)
O&G	2.0(0.7)	2.3(0.8)	9(3.2)	4.0(1.4)	------	2.8(1.0)	6.5(2.3)	------	------	4(1.4)	7.2(2.55)	22(7.7)
NH3-N	------	------	------	------	4.8(1.7)	0.14(0.05)	4.5(1.6)	------	2(0.7)	1.2(0.44)	------	2.3(0.8)
Phenolic Compounds	0.14(0.05)	0.003(0.001)	0.4(0.145)	0.37(0.13)	0.05(0.018)	0.0006 (0.002)	0.06 (0.023)	------	------	0.17(0.06)	------	0.017(0.005)
Sulfide	0.03(0.009)	------	0.2(0.07)	0(0)	0.03(0.010)	0.014 (0.005)	0.05 (0.018)	------	------	------	------	0.20(.07)

Footnotes:
AL-aerated lagoon
AS-activated sludge
DAF-dissolved air flotation
E-equalization
F-filtration
OP-oxidation pond
PP-polishing pond
TF-trickling filter
A-Topping
B-Cracking
C-Petrochemicals
D-Lube
E-Integrated

TABLE 27

Expected Effluents from Petroleum Treatment Processes

PROCESS	PROCESS INFLUENT	EFFLUENT CONCENTRATION, mg/L BOD$_5$	COD	TOC	SS	OIL	PHENOL	AMMONIA	SULFIDE	REFERENCES
1. API Separator	Raw Waste	250-350	260-700	NA	50-200	20-100	6-100	15-150	NA	7,13,30,41,49,59
2. Clarifier	1	45-200	130-450	NA	25-60	5-35	10-40	NA	NA	34,48a,49
3. Dissolved Air Flotation	1	45-200	130-450	NA	25-60	5-20	10-40	NA	NA	13,29,32,48a,49
4. Granular Media Filter	1	40-170	100-400	NA	.5-25	6-20	3-35	NA	NA	17,41,48a,48
5. Oxidation Pond	1	10-60	50-300	NA	20-100	1.6-50	0.01-12	3-50	0-20	18,22,23,31,42,48a, 49,55,75,R18
6. Aerated Lagoon	2,3,4	10-50	50-200	NA	10-80	5-20	0.1-25	4-25	0-0.2	31,39,42a,48a,49, 55,59,R7,R23,R26
7. Activated Sludge	2,3,4	5-50	30-200	20-80	5-50	1-15	0.01-2.0	1-100	0-0.2	13,24,27,30,34,35, 42,48a,49,60,69,72 R8,R20,R24,R25,R27 R28,R29
8. Trickling Filter	1	25-50	80-350	NA	20-70	10-80	0.5-10	25-100	0.5-2	18,30,42,48a,49.
9. Cooling Tower	2,3,4	25-50	47-350	70-150	4.5-100	20-75	.1-2.0	1-30	NA	33,41
10. Activated Carbon	2,3,4	5-100	30-200	NA	10-20	2-20	<1	10-140	NA	17,21,27,48,48a,49, 53,62a
11. Granular Media Filter	5-9	NA	NA	25-61	3-20	3-17	0.35-10	NA	NA	17,48,54
12. Activated Carbon	5-9 and 11	3-10	30-100	1-17	1-15	0.8-2.5	0-0.1	1-100	0-0.2	17,21,27,48,48a,49, 53,62a

A - Data Not Available

TABLE 28

Typical Removal Efficiencies for Oil Refinery Treatment Processes

PROCESS	PROCESS INFLUENT	REMOVAL EFFICIENCY, %								REFERENCES
		BOD_5	COD	TOC	SS	OIL	PHENOL	AMMONIA	SULFIDE	
1. API Separator	Raw Waste	5-40	5-30	NA	10-50	60-99	0-50	NA	NA	7,13,30,41,49,59
2. Clarifier	1	30-60	20-50	NA	50-80	60-95	0-50	NA	NA	34,48a,49
3. Dissolved Air Flotation	1	20-70	10-60	NA	50-85	70-85	10-75	NA	NA	13,29,32,48a,49
4. Filter	1	40-70	20-55	NA	75-95	65-90	5-20	NA	NA	17,41,48a,49
5. Oxidation Pond	1	40-95	30-65	60	20-70	50-90	60-99	0-15	70-100	18,22,23,31,42,48 49,55,75,R18
6. Aerated Lagoon	2,3,4	75-95	60-85	NA	40-65	70-90	90-99	10-45	95-100	31,39,42,48a,49, 55,59,R7,R23,R26
7. Activated Sludge	2,3,4	80-99	50-95	40-90	60-85	80-99	95-99+	33-99	97-100	13,24,R7,30,34,35 42,48a,49,60,69,72 R8,R20,R24,R25,R2 R28,R29
8. Trickling Filter	1	60-85	30-70	NA	60-85	50-80	70-98	15-90	70-100	18,30,42,48a,49
9. Cooling Tower	2,3,4	50-90	40-90	10-70	50-85	60-75	75-99+	60-95	NA	33,41
10. Activated Carbon	2,3,4	70-95	70-90	50-80	60-90	75-95	90-100	7-33	NA	17,21,27,48,48a,49 49,53,62a
11. Filter Granular Media	5-9	NA	NA	50-65	75-95	65-95	5-20	NA	NA	17,48,54
12. Activated Carbon	5-9 plus 11	91-98	86-94	50-80	60-90	70-95	90-99	33-87	NA	17,21,27,48,48a, 49,53,62a

NA - Data Not Available

Dissolved Air Flotation

Dissolved air flotation consists of saturating a portion of the waste water feed, or a portion of the feed or recycled effluent from the flotation unit with air at a pressure of 40 to 60 psig. The waste water or effluent recycle is held at this pressure for 1-5 minutes in a retention tank and then released at atmospheric pressure to the flotation chamber. The sudden reduction in pressure results in the release of microscopic air bubbles which attach themselves to oil and suspended particles in the waste water in the flotation chamber. This results in agglomerates which, due to the entrained air, have greatly-increased vertical rise rates of about 0.5 to 1.0 feet/minute. The floated materials rise to the surface to form a froth layer. Specially designed flight scrapers or other skimming devices continuously remove the froth. The retention time in the flotation chambers is usually about 10-30 minutes. The effectiveness of dissolved air flotation depends upon the attachment of bubbles to the suspended oil and other particles which are to be removed from the waste stream. The attraction between the air bubble and particle is a result of the particle surface and bubble-size distribution.

Chemical flocculating agents, such as salts of iron and aluminum, with or without organic polyelectrolytes, are often helpful in improving the effectiveness of the air flotation process and in obtaining a high degree of clarification.

Dissolved air flotation is used by a number of refineries to treat the effluent from the oil separator. Dissolved air flotation using flocculating agents is also used to treat oil emulsions. The froth skimmed from the flotation tank can be combined with other sludges (such as those from a gravity separator) for disposal. The clarified effluent from a flotation unit generally receives further treatment in a biological unit, prior to discharge. In two refineries, dissolved air flotation is used for clarification of biologically treated effluents (29).

Oxidation Ponds

The oxidation pond is practical where land is plentiful and cheap. An oxidation pond has a large surface area and a shallow depth, usually not exceeding 6 feet. These ponds have long detention periods from 11 to 110 days.

The shallow depth allows the oxidation pond to be operated aerobically without mechanical aerators. The algae in the pond produce oxygen through photosynthesis. This oxygen is then used by the bacteria to oxidize the wastes. Because of the low loadings, little biological sludge is produced and the pond is fairly resistant to uspsets due to shock loadings.

Oxidation ponds are usually used as the major treatment process. Some refineries use ponds as a polishing process after other treatment processes.

Aerated Lagoon

The aerated lagoon is a smaller, deeper oxidation pond equipped with mechanical aerators or diffused air units. The addition of oxygen enables the aerated lagoon to have a higher concentration of microbes than the oxidation pond. The retention time in aerated lagoons is usually shorter, between 3 and 10 days. Most aerated lagoons are operated without final clarification. As a result, biota is discharged in the effluent, causing the effluent to have high BOD_5 and solids concentrations. As the effluent standards become more strict, final clarification will be increasing in use.

Trickling Filter

A trickling filter is an aerobic biological process. It differs from other processes in that the biomass is attached to the bed media, which may be rock, slag, or plastic. The filter works by: 1) adsorption of organics by the biological slime 2) diffusion of air into the biomass; and 3) oxidation of the dissolved organics. When the biomass reaches a certain thickness, part of it sloughs off. When the filter is used as the major treatment process, a clarifier is used to remove the sloughed biomass.

The trickling filter can be used either as the complete treatment system or as a roughing filter. Most applications in the petroleum industry use it as a roughing device to reduce the loading on an activated sludge system.

Bio-Oxidation Tower

The bio-oxidation tower uses a cooling tower to transfer oxygen to a waste water. API (112) has called the bio-oxidation towers a modified activated sludge process, as most of the biomass is suspended in the wastewater. Results from refineries indicate it is a successful process to treat portions or all of a refinery waste water (80, 81, 92).

Activated Sludge

Activated sludge is an aerobic biological treatment process in which high concentrations (1500-3000 mg/L) of newly-grown and recycled microorganisms are suspended uniformly throughout a holding tank to which raw waste waters are added. Oxygen is introduced by mechanical aerators, diffused air systems, or other means. The organic materials in the waste are removed from the aqueous phase by the microbiological growths and stabilized by biochemical synthesis and oxidation reactions. The basic activated sludge process consists of an aeration tank followed by a sedimentation tank. The flocculant microbial growths removed in the sedimentation tank are recycled to the aeration tank to maintain a high concentration of active microorganisms. Although the microorganisms remove almost all of the organic matter from the waste being treated, much of the converted organic matter remains in the system in the form of microbial cells. These cells have a relatively high rate of oxygen demand and must be removed from the treated waste water before discharge. Thus, final sedimentation and recirculation of biological solids are important elements in an activated sludge system.

Sludge is wasted on a continuous basis at a relatively low rate to prevent build-up of excess activated sludge in the aeration tank. Shock organic loads usually result in an overloaded system and poor sludge settling characteristics. Effective performance of activated sludge facilities requires pretreatment to remove or substantially reduce oil, sulfides (which causes toxicity to microorganisms), and phenol concentrations. The pretreatment units most frequently used are: gravity separators and air flotation units to remove oil; and sour water strippers to remove sulfides, mercaptans, and phenol. Equalization also appears necessary to prevent shock loadings from upsetting the aeration basin. Because of the high rate and degree of organic stabilization possible with activated sludge, application of this process to the treatment of refinery waste waters has been increasing rapidly in recent years.

Many variations of the activated sludge process are currently in use. Examples include: the tapered aeration process, which has greater air addition at the influent where the oxygen demand is the highest; step aeration, which introduces the influent waste water along the length of the aeration tank; and contact stabilization, in which the return sludge to the aeration tank is aerated for 1-5 hours. The contact stabilization process is useful where the oxygen demand is in the suspended or colloidal form. The completely mixed activated sludge plant uses large mechanical mixers to mix the influent with the contents of the aeration basin, decreasing the possibility of upsets due to shock loadings. The Pasveer ditch is a variation of the completely mixed activated sludge process that is widely used in Europe. Here brushes are used to provide aeration and mixing in a narrow oval ditch. The advantage of this process is that the concentration of the biota is higher than in the conventional activated sludge process, and the wasted sludge is easy to dewater. There is at least one refinery using the Pasveer ditch type system.

The activated sludge process has several disadvantages. Because of the amount of mechanical equipment involved, its operating and maintenance costs are higher than other biological systems. The small volume of the aeration basin makes the process more subject to upsets than either oxidation ponds or aerated lagoons.

As indicated in Table 25, the activated sludge process is capable of achieving very low concentrations of BOD5, COD, TSS, and oil, dependent upon the influent waste loading and the particular design basis. Reported efficiencies for BOD5 removal are in the range of 80 to 99 percent.

Physical-Chemical Treatment

Physical-chemical treatment refers to treatment processes that are non-biological in nature. There are two types of physical-chemical processes; those that reduce the volume of water to be treated (vapor compression evaporators, reverse osmosis, etc.), and those that reduce the concentration of the pollutants (activated carbon).

Physical-chemical (P-C) processes require less land than biological processes. P-C processes are not as susceptible to upset due to shock loading as are biological processes. Another advantage of P-C is that much smaller amounts of sludge are produced.

Flow Reduction Systems

Flow reduction systems produce two effluents, one of relatively pure water and one a concentrated brine. The pure water stream can be reused within the refinery resulting in a smaller effluent flow. The brine is easier to treat as it is highly concentrated. Both of the processes described herein have been demonstrated on small flows only and at present the costs involved are extremely high (45, 52, 93).

In the vapor compression evaporator the waste water flows over heat transfer surfaces. The steam generated enters a compressor where the temperature is raised to a few degrees above the boiling point of the waste water. The compressed steam is used to evaporate more waste water while being condensed. The condensed steam is low in dissolved solids. The major process costs are the costs of electrical power, which is approximately $1.0/1000 gallons of clean water (93).

The reverse osmosis process uses high pressures (400-800 psig) to force water through a semi-permeable membrane. The membrane allows the water to pass through, but contains the other constituents in the waste water. Currently available membranes tend to foul and blind, requiring frequent cleaning and replacement. Until this problem is corrected, reverse osmosis is not a practicable process. The operating cost for a reverse osmosis unit is approximately 20-30¢/1000 gallons (45, 95).

Granular Media Filters

There are several types of granular media filters: sand, dual media, and multimedia. These filters operate in basically the same way, the only difference being the filter media. The sand filter uses relatively uniform grade of sand resting on a coarser material. The dual media filter has a course layer of coal above a fine layer of sand. Both types of filters have the problem of keeping the fine particles on the bottom. This problem is solved by using a third very heavy, very fine material, (usually garnet) beneath the coal and sand.

As the water passes down through a filter, the suspended matter is caught in the pores. When the pressure drop through the filter becomes excessive, the flow through the filter is reversed for removal of the collected solids loading. The backwash cycle occurs approximately once a day, depending on the loading, and usually lasts for 5-8 minutes. Most uses of sand filters have been for removing oil and solids prior to an activated carbon unit. There is one refinery that uses a mixed media filter on the effluent from a biological system. Granular media filters are shown to be capable of consistently operated with extremely low TSS and oil effluent discharges, on the order of 5-10 mg/L.

Activated Carbon

The activated carbon (AC) process utilizes granular activated carbon to adsorb pollutants from waste water. The adsorption is a function of the molecular size and polarity of the adsorbed substance. Activated carbon preferentially adsorbs large organic molecules that are non-polar.

An AC unit follows a solids removal process, usually a sand filter which prevents plugging of the carbon pores. From the filter the water flows to a bank of carbon columns arranged in series or parallel. As the water flows through the columns the pollutants are adsorbed by the carbon, gradually filling the pores. At intervals, portions of the carbon are removed to a furnace where the adsorbed substances are burnt off. The regenerated carbon is reused in the columns, with some makeup added, because of handling and efficiency losses.

Activated carbon processes currently have only limited usage in the refining industry. However, there are new installations in the planning construction stages. The increasing use of activated carbon has occured because activated carbon can remove organic materials on an economically competitive basis with biological treatment. Activated carbon regeneration furnaces have high energy requirements.

Sludge Handling and Disposal

Digestion

Digestion is usually used preceding the other sludge concentration and disposal methods. The purpose of digestion is to improve the dewatering of the sludge. Digestion can occur aerobically or anaerobically. During digestion, bacteria decompose the organic material in the sludge producing methane, carbon dioxide and water. At the end of the digestion process, the sludge is stable and non-decomposable.

Vacuum Filtration

The various vacuum filters, usually a revolving drum, use a vacuum to dewater the sludge. The revolving drum type has a vacuum applied against a cloth. The water passes through the cloth and returns to the influent of the treatment plant. The sludge remains on the drum until it is scraped off with a knife.

Centrifugation

Centrifugation uses high speed rotation to separate sludge and water. The heavier sludge moves to the outside and is conveyed to one end, where it is collected for final disposal. The water flows out the opposite end and is returned to the treatment plant.

Sludge Disposal

From any waste water treatment plant, the sludge must be disposed of. The methods used are landfilling, landfarming, barging to sea, and incineration.

Landfilling

A landfill operation requires a large amount of land. Before landfilling, the sludge should be digested to avoid odor problems. The sludge is disposed of in an excavation site. After each batch is disposed of, it is covered with a layer of earth. When the site is filled to capacity it is covered with a thick layer of earth.

The largest problem of industrial landfills is the pollution to ground and surface waters by leaching. Leaching occurs when water percolates through the landfill. As it drains through the landfill site, the water carries with it dissolved and suspended solids and organic matter. This water can then contaminate underground or surface streams it comes in contact with.

Incineration

Incineration is gradually complementing landfills as a method of sludge disposal. The principal process is fluid bed incineration. In this process, a bed of sand is preheated with hot air to 482-538°C (900 - 1000°F). Torch oil is then used to raise the bed temperature to 649 - 705°C (1200 - 1300°F). At this point waste water sludge and/or sludge is introduced and the torch oil is stopped. The solid products of combustion remain in the bed which is a gradually withdrawn to maintain a constant bed height. Eventually, the bed will be composed of only ash.

The sludge fed to the incinerator usually contains inorganic as well as organic material. However, the sludge must contain a minimum amount of organics to maintain the combustion process. One refinery (26) suggests a minimum of 1,930,000 cal/cu m (29,000 Btu/gal) of sludge heating value is necessary to maintain the combustion process.

SECTION VIII

COST, ENERGY, AND NON-WATER QUALITY ASPECTS

The first part of this section summarizes the costs (necessarily generalized) and effectiveness of end-of-pipe control technology for BPCTCA and BATEA and BADT-NSPS effluent limitations. Treatment costs for small, medium, and large refineries in each subcategory have been estimated for the technologies considered. The expected annual costs for existing plants in the petroleum refining industry in 1977 consistent with BPCTCA effluent limitations are estimated at $225 million (end-of-pipe treatment only). For 1983, consistent with BATEA effluent limitations, the estimated additional annual costs are estimated at $250 million (end-of-pipe treatment only). For BADT-NSPS the annual cost is estimated at $26 million. These costs are summarized by subcategory in Table 29.

The effect of plant size relative to annual costs can be seen in Table 30 where the annual costs are summarized for application of BPCTCA and BATEA to small, medium, and large refineries in each subcategory. The cost, energy, and nonwater quality aspects of in-plant controls are intimately related to the specific processes for which they are developed. Although there are general cost and energy requirements for equipment items (e.g. surface air coolers), these correlations are usually expressed in terms of specific design parameters, such as the required heat transfer area. Such parameters are related to the production rate and specific situations that exist at a particular production site.

There is a wide variation in refinery sizes. When these size ranges are superimposed on the large number of processes within each subcategory, it is apparent that many detailed designs would be required to develop a meaningful understanding of the economic impact of process modifications. The decision to attain the limitations through in-plant controls or by end-of-pipe treatment should be left up to individual manufacturers. Therefore, a series of possible designs for the end-of-pipe treatment models is provided.

Alternative Treatment Technologies

The range of components used or needed for either best practicable or best available technology have been combined into five alternative end-of-pipe treatment steps, which are as follows:

A. Initial treatment, consisting of dissolved air flotation, equalization, neutralization, and nutrient (phosphoric acid) feed facilities.

TABLE 29

Estimated Total Annual Costs for End-of-Pipe Treatment Systems for the Petroleum Refining Industry (Existing Refineries)

Subcategory		Total Annual Cost, $ Million 1977	 1983
Topping		$14.2	$16.5
Cracking		81.3	92.5
Petrochemical		53.9	50.0
Lube		70.1	66.2
Integrated		35.5	24.8
	Industry Total	$255.0	$250.0

TABLE 30

Summary of End-of-Pipe Waste Water Treatment Costs for Representative Plants in the Petroleum Refining Industry

Subcategory	Representative Refinery Size		Annual Level 1 Costs		Annual Additional Level 11 Costs	
	1000 m^3/day	1000 BBL/day	\$/1000 m^3	\$/1000 gal	\$/1000 m^3	\$/1000 gal
Topping	0.318	2	0.066	17.31	0.070	18.41
	1.11	7	0.030	7.86	0.034	9.06
	2.4	15	0.018	4.87	0.023	5.97
Cracking	2.4	15	0.014	3.78	0.019	4.90
	11.9	75	0.007	1.84	0.008	2.20
	23.8	150	0.006	1.62	0.006	1.47
Petrochemical	4.0	25	0.009	2.32	0.010	2.65
	15.9	100	0.007	1.78	0.006	1.63
	31.8	200	0.005	1.35	0.005	1.20
Lube	4.0	25	0.009	2.33	0.010	2.57
	17.5	110	0.006	1.50	0.006	1.51
	39.8	250	0.005	1.25	0.004	0.93
Integrated	9.8	65	0.006	1.67	0.006	1.53
	23.0	152	0.005	1.28	0.005	1.05
	49.0	326	0.005	1.13	0.003	0.65

B. Biological treatment, consisting of acitvated sludge units, thickness, digestors, and dewatering facilities.

C. Granular media filtration, consisting of filter systems and associated equipment.

D. Physical-chemical treatment facilities consisting of activated carbon adsorption.

E. Alternative Biological treatment, consisting of aerated lagoon facilities.

Tables 31 through 45 are summaries of the costs of major treatment steps required to achieve different levels of technology for small, medium, and large refineries in each subcategory; using median raw waste loads and median "good water use" flow rates, for the end-of-pipe treatment models.

BPCTCA Treatment Systems Used for the Economic Evaluation

A general flow schematic for the BPCTCA waste water treatment facilities is shown in Figure 6. A summary of the general design basis is presented in Table 46 and a summary of the treatment system effluent limitations for each subcategory is presented in Tables 1-6.

BATEA treatment Systems Used for the Economic Evaluation

BATEA treatment facilities are basically added on to the discharge pipe from BPCTCA facilities. It is expected that flows will be reduced slightly by the application of BATEA in-plant technology, so that the activated carbon treatment unit may treat a smaller hydraulic load. However, the activated carbon system was sized for the same flow basis as in BPCTCA technology in order to establish a conservative basis for economic evaluation of proposed effluent limitations.

A general flow schematic diagram for the BATEA waste water treatment facilities is shown in Figure 7. A summary of the general design basis is presented in Table 47. and a summary of the treatment system effluent limitations for each subcategory is presented in Tables 1-6.

TABLE 31

WATER EFFLUENT TREATMENT COSTS

PETROLEUM REFINING INDUSTRY

TOPPING SUBCATEGORY

Refinery Capacity 1000 cubic meters/day (1000 bbl/day)	0.318 (2)
Wastewater Flow cubic meters/cubic meter of feedstock (gal/bbl)	0.477 (20)
Treatment Plant Size 1000 cubic meters/day (MGD)	0.146 (0.040)

Costs in $1000	Alternative Treatment Steps			
	A	B	C	D
Initial Investment	210	174	60	390
ANNUAL COSTS:				
Capital Costs (10%)	21.0	17.4	6.0	39
Depreciation (20%)	42.0	34.8	12.0	78
Operating Costs	14.6	12.4	4.2	72.5
Energy	1.0	7.8	1.0	6.5
Total Annual Costs	78.6	72.4	23.2	196.0

Effluent Quality

	Raw Waste Load kg/1000 cu m (lb/1000 bbl)	Resulting Effluent Levels (Design Average kg/1000 cu m)		
		B	C	D
BOD5	13.3 (4.7)	7.1	-	1.2
COD	36.8 (13)	37.6	-	5.0
Oil & Grease	8.2 (2.9)	3.3	2.3	0.25
Phenolics	0.034 (0.012)	0.048	-	0.0051
Sulfide	0.054 (0.019)	0.048	-	0.025
Ammonia	3.7 (1.3)	0.85	-	0.34
Suspended Solids	11.6 (4.1)	9.6	4.8	1.2
Total Chromium	0.20 (0.07)	0.24	0.119	0.062

TABLE 32

WATER EFFLUENT TREATMENT COSTS

PETROLEUM REFINING INDUSTRY

TOPPING SUBCATEGORY

Refinery Capacity 1000 cubic meters/day (1000 bbl/day)	1.11 (7)
Wastewater Flow cubic meters/cubic meter of feedstock (gal/bbl)	0.47 (20)
Treatment Plant Size 1000 cubic meters/day (MGD)	0.51 (0.140)

Costs in $1000	Alternative Treatment Steps			
	A	B	C	D
Initial Investment	320	290	102	815
ANNUAL COSTS:				
Capital Costs (10%)	32.0	29.0	10.2	81.5
Depreciation (20%)	64.0	58.0	20.4	163.0
Operating Costs	23.0	19.0	6.0	89.0
Energy	2.0	12.0	2.0	9.0
Total Annual Costs	121.0	118.0	38.6	342.5

Effluent Quality

	Raw Waste Load kg/1000 cu m (lb/1000 bbl)	Resulting Effluent Levels (Design Average kg/1000 cu m)		
		B	C	D
BOD5	13.3 (4.7)	7.1	-	1.2
COD	36.8 (13)	37.6	-	5.0
Oil & Grease	8.2 (2.9)	3.3	2.3	0.25
Phenolics	0.034 (0.012)	0.048	-	0.0051
Sulfide	0.054 (0.019)	0.048	-	0.025
Ammonia	3.7 (1.3)	0.85	-	0.34
Suspended Solids	11.6 (4.1)	9.6	4.8	1.2
Total Chromium	0.20 (0.07)	0.24	0.119	0.062

TABLE 33

WATER EFFLUENT TREATMENT COSTS

PETROLEUM REFINING INDUSTRY

TOPPING SUBCATEGORY

Refinery Capacity 1000 cubic meters/day (1000 bbl/day)	2.4 (15)
Wastewater Flow cubic meters/cubic meter of feedstock (gal/bbl)	0.47 (20)
Treatment Plant Size 1000 cubic meters/day (MGD)	1.1 (0.30)

Costs in $1000	Alternative Treatment Steps			
	A	B	C	D
Initial Investment	378	400	150	1257
ANNUAL COSTS:				
Capital Costs (10%)	37.8	40.0	15.0	126.0
Depreciation (20%)	75.6	80.0	30.0	252.0
Operating Costs	28.0	26.0	17.0	101.0
Energy	3.0	19.0	2.0	10.0
Total Annual Costs	144.4	165.0	64.0	489.0

Effluent Quality

	Raw Waste Load kg/1000 cu m (lb/1000 bbl)	Resulting Effluent Levels (Design Average kg/1000 cu m)		
		B	C	D
BOD5	13.3 (4.7)	7.1	-	1.2
COD	36.8 (13)	37.6	-	5.0
Oil & Grease	8.2 (2.9)	3.3	2.3	0.25
Phenolics	0.034 (0.012)	0.048	-	0.0051
Sulfide	0.054 (0.019)	0.048	-	0.025
Ammonia	3.7 (1.3)	0.85	-	0.34
Suspended Solids	11.6 (4.1)	9.6	4.8	1.2
Total Chromium	0.20 (0.07)	0.24	0.119	0.062

TABLE 34

WATER EFFLUENT TREATMENT COSTS

PETROLEUM REFINING INDUSTRY

CRACKING SUBCATEGORY

Refinery Capacity 1000 cubic meters/day (1000 bbl/day)	2.4 (15)
Wastewater Flow cubic meters/cubic meter of feedstock (gal/bbl)	0.596 (25)
Treatment Plant Size 1000 cubic meters/day (MGD)	1.37 (0.375)

Costs in $1000	Alternative Treatment Steps			
	A	B	C	D
Initial Investment	405	455	158	1458
ANNUAL COSTS:				
Capital Costs (10%)	40.5	45.5	15.8	146.0
Depreciation (20%)	81.0	91.0	31.6	292.0
Operating Costs	29.0	30.0	11.0	106.0
Energy	2.0	21.0	3.0	10.0
Total Annual Costs	152.5	187.5	61.4	554.0

Effluent Quality

	Raw Waste Load kg/1000 cu m (lb/1000 bbl)	Resulting Effluent Levels (Design Average kg/1000 cu m)		
		B	C	D
BOD5	72.5 (25)	8.8	-	1.6
COD	216.0 (76)	67.9	-	9.6
Oil & Grease	31.0 (10.9)	3.9	2.8	0.34
Phenolics	3.95 (1.4)	0.059	-	0.0065
Sulfide	1.0 (0.35)	0.059	-	0.045
Ammonia	28.0 (9.9)	5.7	-	2.8
Suspended Solids	17.8 (6.3)	11.8	5.9	1.6
Total Chromium	0.25 (0.09)	0.3	0.147	0.05

TABLE 35

WATER EFFLUENT TREATMENT COSTS

PETROLEUM REFINING INDUSTRY

CRACKING SUBCATEGORY

Refinery Capacity 1000 cubic meters/day (1000 bbl/day)	11.9 (75)
Wastewater Flow cubic meters/cubic meter of feedstock (gal/bbl)	0.596 (25)
Treatment Plant Size 1000 cubic meters/day (MGD)	6.8 (1.875)

Costs in $1000	Alternative Treatment Steps			
	A	B	C	D
Initial Investment	950	1760	290	3600
ANNUAL COSTS:				
Capital Costs (10%)	95.0	176.0	29.0	360.0
Depreciation (20%)	190.0	352.0	58.0	720.0
Operating Costs	64.0	86.0	20.0	152.0
Energy	8.0	59.0	7.0	25.0
Total Annual Costs	357.0	63.0	114.0	125.0

Effluent Quality

	Raw Waste Load kg/1000 cu m (lb/1000 bbl)	Resulting Effluent Levels (Design Average kg/1000 cu m)		
		B	C	D
BOD5	72.5 (25)	8.8	-	1.6
COD	216.0 (76)	67.9	-	9.6
Oil & Grease	31.0 (10.9)	3.9	2.8	0.34
Phenolics	3.95 (1.4)	0.059	-	0.0065
Sulfide	1.0 (0.35)	0.059	-	0.045
Ammonia	28.0 (9.9)	5.7	-	2.8
Suspended Solids	17.8 (6.3)	11.8	5.9	1.6
Total Chromium	0.25 (0.09)	0.3	0.147	0.05

TABLE 36

WATER EFFLUENT TREATMENT COSTS

PETROLEUM REFINING INDUSTRY

CRACKING SUBCATEGORY

Refinery Capacity 1000 cubic meters/day (1000 bbl/day)	23.8 (150)
Wastewater Flow cubic meters/cubic meter of feedstock (gal/bbl)	0.596 (25)
Treatment Plant Size 1000 cubic meters/day (MGD)	13.7 (3.75)

Costs in $1000	Alternative Treatment Steps			
	A	B	C	D
Initial Investment	1460	3080	415	5370
ANNUAL COSTS:				
Capital Costs (10%)	146.0	308.0	41.5	537.0
Depreciation (20%)	292.0	616.0	83.0	1074.0
Operating Costs	119.0	236.0	31.0	211.0
Energy	17.0	113.0	15.0	44.0
Total Annual Costs	574.0	123.0	180.5	1866.0

Effluent Quality

	Raw Waste Load kg/1000 cu m (lb/1000 bbl)	Resulting Effluent Levels (Design Average kg/1000 cu m)		
		B	C	D
BOD5	72.5 (25)	8.8	-	1.6
COD	216.0 (76)	67.9	-	9.6
Oil & Grease	31.0 (10.9)	3.9	2.8	0.34
Phenolics	3.95 (1.4)	0.059	-	0.0065
Sulfide	1.0 (0.35)	0.059	-	0.045
Ammonia	28.0 (9.9)	5.7	-	2.8
Suspended Solids	17.8 (6.3)	11.8	5.9	1.6
Total Chromium	0.25 (0.09)	0.3	0.147	0.05

TABLE 37

WATER EFFLUENT TREATMENT COSTS

PETROLEUM REFINING INDUSTRY

PETROCHEMICAL SUBCATEGORY

Refinery Capacity 1000 cubic meters/day (1000 bbl/day)	4.0 (25)
Wastewater Flow cubic meters/cubic meter of feedstock (gal/bbl)	0.715 (30)
Treatment Plant Size 1000 cubic meters/day (MGD)	2.7 (0.75)

Costs in \$1000	Alternative Treatment Steps			
	A	B	C	D
Initial Investment	530	720	195	2050
ANNUAL COSTS:				
Capital Costs (10%)	53.0	72.0	19.5	205.0
Depreciation (20%)	106.0	144.0	39.0	410.0
Operating Costs	39.0	48.0	15.0	125.0
Energy	5.0	34.0	4.0	16.0
Total Annual Costs	203.0	298.0	7.5	56.0

Effluent Quality

	Raw Waste Load kg/1000 cu m (lb/1000 bbl)	Resulting Effluent Levels (Design Average kg/1000 cu m)		
		B	C	D
BOD5	173.0 (60)	10.8	-	2.2
COD	460.0 (162)	67.9	-	10.8
Oil & Grease	52.6 (18.5)	5.1	3.7	0.45
Phenolics	7.6 (2.7)	0.071	-	0.0091
Sulfide	0.9 (0.3)	0.071	-	0.045
Ammonia	35.0 (12.4)	7.1	-	2.8
Suspended Solids	47.7 (17)	14.2	7.1	2.2
Total Chromium	0.30 (0.107)	0.35	0.178	0.11

TABLE 38

WATER EFFLUENT TREATMENT COSTS

PETROLEUM REFINING INDUSTRY

PETROCHEMICAL SUBCATEGORY

Refinery Capacity 1000 cubic meters/day (1000 bbl/day)	15.9 (100)
Wastewater Flow cubic meters/cubic meter of feedstock (gal/bbl)	0.715 (30)
Treatment Plant Size 1000 cubic meters/day (MGD)	10.9 (3.0)

Costs in $1000	Alternative Treatment Steps A	 B	 C	 D
Initial Investment	1260	2700	360	4700
ANNUAL COSTS:				
Capital Costs (10%)	126.0	270.0	36.0	470.0
Depreciation (20%)	252.0	540.0	72.0	940.0
Operating Costs	98.0	203.0	29.0	192.0
Energy	15.0	93.0	12.0	38.0
Total Annual Costs	491.0	1106.0	149.0	1640.0

Effluent Quality

	Raw Waste Load kg/1000 cu m (lb/1000 bbl)	Resulting Effluent Levels (Design Average kg/1000 cu m) B	 C	 D
BOD5	173.0 (60)	10.8	-	2.2
COD	460.0 (162)	67.9	-	10.8
Oil & Grease	52.6 (18.5)	5.1	3.7	0.45
Phenolics	7.6 (2.7)	0.071	-	0.0091
Sulfide	0.9 (0.3)	0.071	-	0.045
Ammonia	35.0 (12.4)	7.1	-	2.8
Suspended Solids	47.7 (17)	14.2	7.1	2.2
Total Chromium	0.30 (0.107)	0.35	0.178	0.11

TABLE 39

WATER EFFLUENT TREATMENT COSTS

PETROLEUM REFINING INDUSTRY

PETROCHEMICAL SUBCATEGORY

Refinery Capacity 1000 cubic meters/day (1000 bbl/day)	31.8 (200)
Wastewater Flow cubic meters/cubic meter of feedstock (gal/bbl)	0.715 (30)
Treatment Plant Size 1000 cubic meters/day (MGD)	21.9 (6.0)

Costs in $1000

	Alternative Treatment Steps			
	A	B	C	D
Initial Investment	1830	4070	430	6650
ANNUAL COSTS:				
Capital Costs (10%)	183.0	407.0	43.0	665.0
Depreciation (20%)	366.0	814.0	86.0	1330.0
Operating Costs	145.0	329.0	37.0	270.0
Energy	25.0	155.0	20.0	60.0
Total Annual Costs	719.0	1648.0	186.0	2325.0

Effluent Quality

	Raw Waste Load kg/1000 cu m (lb/1000 bbl)	Resulting Effluent Levels (Design Average kg/1000 cu m)		
		B	C	D
BOD5	173.0 (60)	10.8	-	2.2
COD	460.0 (162)	67.9	-	10.8
Oil & Grease	52.6 (18.5)	5.1	3.7	0.45
Phenolics	7.6 (2.7)	0.071	-	0.0091
Sulfide	0.9 (0.3)	0.071	-	0.045
Ammonia	35.0 (12.4)	7.1	-	2.8
Suspended Solids	47.7 (17)	14.2	7.1	2.2
Total Chromium	0.30 (0.107)	0.35	0.178	0.11

TABLE 40

WATER EFFLUENT TREATMENT COSTS

PETROLEUM REFINING INDUSTRY

LUBE SUBCATEGORY

Refinery Capacity 1000 cubic meters/day (1000 bbl/day)	4.0 (25)
Wastewater Flow cubic meters/cubic meter of feedstock (gal/bbl)	1.07 (45)
Treatment Plant Size 1000 cubic meters/day (MGD)	4.1 (1.125)

Costs in $1000	Alternative Treatment Steps			
	A	B	C	D
Initial Investment	690	1120	220	2700
ANNUAL COSTS:				
Capital Costs (10%)	69.0	112.0	22.0	270.0
Depreciation (20%)	138.0	224.0	44.0	540.0
Operating Costs	62.0	72.0	20.0	139.0
Energy	6.0	47.0	5.0	20.0
Total Annual Costs	275.0	455.0	91.0	969.0

Effluent Quality

	Raw Waste Load kg/1000 cu m (lb/1000 bbl)	Resulting Effluent Levels (Design Average kg/1000 cu m)		
		B	C	D
BOD5	215.0 (76)	15.8	-	3.7
COD	538.0 (190)	116.0	-	20.0
Oil & Grease	119.0 (42)	7.5	5.4	0.71
Phenolics	8.2 (2.9)	0.108	-	0.014
Sulfide	0.014 (0.005)	0.108	-	0.071
Ammonia	35.0 (12.4)	7.1	-	2.8
Suspended Solids	71.0 (25)	22.0	10.8	3.7
Total Chromium	0.45 (0.16)	0.50	0.266	0.18

TABLE 41

WATER EFFLUENT TREATMENT COSTS

PETROLEUM REFINING INDUSTRY

LUBE SUBCATEGORY

Refinery Capacity 1000 cubic meters/day (1000 bbl/day)	17.5 (45)
Wastewater Flow cubic meters/cubic meter of feedstock (gal/bbl)	1.07 (45)
Treatment Plant Size 1000 cubic meters/day (MGD)	18.0 (4.95)

Costs in $1000	Alternative Treatment Steps			
	A	B	C	D
Initial Investment	1650	3720	420	6100
ANNUAL COSTS:				
Capital Costs (10%)	165.0	372.0	42.0	610.0
Depreciation (20%)	330.0	744.0	84.0	1220.0
Operating Costs	129.0	285.0	35.0	236.0
Energy	20.0	135.0	17.0	52.0
Total Annual Costs	644.0	1536.0	178.0	2118.0

Effluent Quality

	Raw Waste Load kg/1000 cu m (lb/1000 bbl)	Resulting Effluent Levels (Design Average kg/1000 cu m)		
		B	C	D
BOD5	215.0 (76)	15.8	-	3.7
COD	538.0 (190)	116.0	-	20.0
Oil & Grease	119.0 (42)	7.5	5.4	0.71
Phenolics	8.2 (2.9)	0.108	-	0.014
Sulfide	0.014 (0.005)	0.108	-	0.071
Ammonia	35.0 (12.4)	7.1	-	2.8
Suspended Solids	71.0 (25)	22.0	10.8	3.7
Total Chromium	0.45 (0.16)	0.50	0.266	0.18

TABLE 42

WATER EFFLUENT TREATMENT COSTS

PETROLEUM REFINING INDUSTRY

LUBE SUBCATEGORY

Refinery Capacity 1000 cubic meters/day (1000 bbl/day)	39.8 (250)
Wastewater Flow cubic meters/cubic meter of feedstock (gal/bbl)	1.07 (45)
Treatment Plant Size 1000 cubic meters/day (MGD)	41.0 (11.25)

Costs in $1000	Alternative Treatment Steps			
	A	B	C	D
Initial Investment	3220	7720	600	9500
ANNUAL COSTS:				
Capital Costs (10%)	322.0	772.0	60.0	950.0
Depreciation (20%)	644.0	1544.0	120.0	1900.0
Operating Costs	256.0	595.0	48.0	370.0
Energy	45.0	245.0	35.0	95.0
Total Annual Costs	1267.0	3156.0	263.0	3315.0

Effluent Quality

	Raw Waste Load kg/1000 cu m (lb/1000 bbl)	Resulting Effluent Levels (Design Average kg/1000 cu m)		
		B	C	D
BOD5	215.0 (76)	15.8	-	3.7
COD	538.0 (190)	116.0	-	20.0
Oil & Grease	119.0 (42)	7.5	5.4	0.71
Phenolics	8.2 (2.9)	0.108	-	0.014
Sulfide	0.014 (0.005)	0.108	-	0.071
Ammonia	35.0 (12.4)	7.1	-	2.8
Suspended Solids	71.0 (25)	22.0	10.8	3.7
Total Chromium	0.45 (0.16)	0.50	0.266	0.18

TABLE 43

WATER EFFLUENT TREATMENT COSTS

PETROLEUM REFINING INDUSTRY

INTEGRATED SUBCATEGORY

Refinery Capacity 1000 cubic meters/day (1000 bbl/day)	9.8 (65)
Wastewater Flow cubic meters/cubic meter of feedstock (gal/bbl)	1.14 (48)
Treatment Plant Size 1000 cubic meters/day (MGD)	11.4 (3.12)

Costs in $1000	Alternative Treatment Steps			
	A	B	C	D
Initial Investment	1270	3040	242	4900
ANNUAL COSTS:				
Capital Costs (10%)	127.0	304.0	24.0	490.0
Depreciation (20%)	254.0	608.0	48.0	980.0
Operating Costs	103.0	243.0	21.0	206.0
Energy	20.0	106.0	15.0	43.0
Total Annual Costs	504.0	1261.0	108.0	1719.0

Effluent Quality

	Raw Waste Load kg/1000 cu m (lb/1000 bbl)	Resulting Effluent Levels (Design Average kg/1000 cu m)		
		B	C	D
BOD5	195.0 (69)	17.0	-	4.2
COD	325.0 (115)	125.0	-	23.7
Oil & Grease	74.0 (26)	8.4	5.7	0.85
Phenolics	3.7 (1.32)	0.113	-	0.017
Sulfide	2.0 (0.7)	0.113	-	0.085
Ammonia	35.0 (12.4)	7.1	-	2.8
Suspended Solids	57.0 (20.3)	22.0	11.3	4.2
Total Chromium	0.48 (0.17)	0.57	0.283	0.22

TABLE 44

WATER EFFLUENT TREATMENT COSTS
PETROLEUM REFINING INDUSTRY
INTEGRATED SUBCATEGORY

Refinery Capacity 1000 cubic meters/day (1000 bbl/day)	23.0 (152)
Wastewater Flow cubic meters/cubic meter of feedstock (gal/bbl)	1.14 (48)
Treatment Plant Size 1000 cubic meters/day (MGD)	26.6 (7.3)

Costs in $1000	Alternative Treatment Steps			
	A	B	C	D
Initial Investment	2340	5440	434	7860
ANNUAL COSTS:				
Capital Costs (10%)	234.0	544.0	43.0	786.0
Depreciation (20%)	468.0	1088.0	86.0	1572.0
Operating Costs	203.0	470.0	38.0	329.0
Energy	36.0	188.0	21.0	68.0
Total Annual Costs	941.0	2290.0	188.0	2755.0

Effluent Quality

	Raw Waste Load kg/1000 cu m (lb/1000 bbl)	Resulting Effluent Levels (Design Average kg/1000 cu m)		
		B	C	D
BOD5	195.0 (69)	17.0	-	4.2
COD	325.0 (115)	125.0	-	23.7
Oil & Grease	74.0 (26)	8.4	5.7	0.85
Phenolics	3.7 (1.32)	0.113	-	0.017
Sulfide	2.0 (0.7)	0.113	-	0.085
Ammonia	35.0 (12.4)	7.1	-	2.8
Suspended Solids	57.0 (20.3)	22.0	11.3	4.2
Total Chromium	0.48 (0.17)	0.57	0.283	0.22

TABLE 45

WATER EFFLUENT TREATMENT COSTS

PETROLEUM REFINING INDUSTRY

INTEGRATED SUBCATEGORY

Refinery Capacity 1000 cubic meters/day (1000 bbl/day)	49.0 (326)
Wastewater Flow cubic meters/cubic meter of feedstock (gal/bbl)	1.14 (48)
Treatment Plant Size 1000 cubic meters/day (MGD)	56.8 (15.6)

Costs in $1000	Alternative Treatment Steps			
	A	B	C	D
Initial Investment	4410	10100	820	10500
ANNUAL COSTS:				
Capital Costs (10%)	441.0	1010.0	82.0	1050.0
Depreciation (20%)	882.0	2020.0	164.0	2100.0
Operating Costs	381.0	885.0	71.0	439.0
Energy	69.0	354.0	52.0	107.0
Total Annual Costs	1773.0	4269.0	369.0	3696.0

Effluent Quality

	Raw Waste Load kg/1000 cu m (lb/1000 bbl)	Resulting Effluent Levels (Design Average kg/1000 cu m)		
		B	C	D
BOD5	195.0 (69)	17.0	-	4.2
COD	325.0 (115)	125.0	-	23.7
Oil & Grease	74.0 (26)	8.4	5.7	0.85
Phenolics	3.7 (1.32)	0.113	-	0.017
Sulfide	2.0 (0.7)	0.113	-	0.085
Ammonia	35.0 (12.4)	7.1	-	2.8
Suspended Solids	57.0 (20.3)	22.0	11.3	4.2
Total Chromium	0.48 (0.17)	0.57	0.283	0.22

FIGURE 6

BPCTCA - Wastewater Treatment System

MODEL SYSTEM USED FOR THE ECONOMIC EVALUATION

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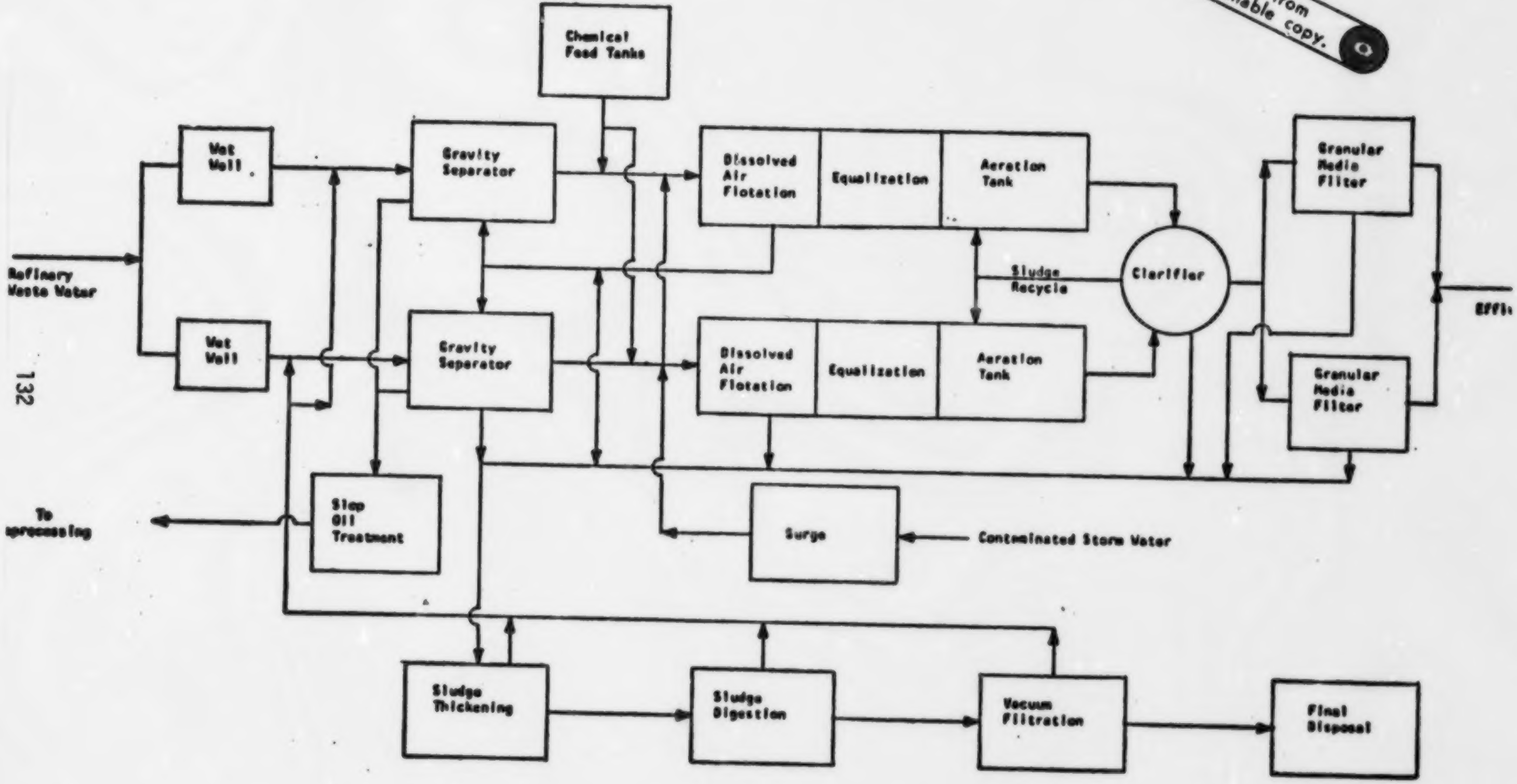

TABLE 46

BPCTCA - END OF PIPE TREATMENT SYSTEM
MODEL USE FOR THE ECONOMIC EVALUATION
DESIGN SUMMARY

Treatment System Hydraulic Loading

Treatment system hydraulic loadings are sized to represent the projected waste water flows from small, average, and large refineries in each subcategory. The flow range used in these estimates ranges from 95 to 38,000 m^3/day (25,000 gpd to 10,000,000 gpd).

Dissolved Air Flotation

The flotation units are sized for an overflow rate of 570 m^3/day/m^2 (1400 gpd/sq.ft)

Pump Station

Capacity to handle 200 percent of the average hydraulic flow.

Equalization

One day detention time is provided. Floating mixers are provided to keep the contents completely mixed.

Neutralization

The two-stage neutralization basin is sized on the basis of an average detention time of twenty minutes. The lime-handling facilities are sized to add 1,000 lbs. of hydrated lime per mgd of waste water, to adjust the pH. Bulk-storage facilities (based on 15 days usage) or bag storage is provided, depending on plant size. Lime addition is controlled by two pH probes, one in each basin. The lime slurry is added to the neutralization basin from a lime slurry recirculation loop. The lime-handling facilities are enclosed in a building.

Nutrient Addition

Facilities are provided for the addition of phosphoric acid to the biological system in order to maintain the ratio of BOD:P at 100:1.

Aeration Basin

Platform-mounted mechanical aerators are provided in the aeration basin. In addition, walkways are provided to all aerators for fan access and maintenance. The following data were used in sizing the aerators.

Oxygen utilization	1.5 kg O_2/kg BOD

	(1.5 lbs O_2/lb. BOD) removed
L	0.8
B	0.9
Waste water temperature	20°C
Oxygen transfer	1.6 kg (3.5 lbs.) O_2/hr./shaft HP at 20°C and zero D.O. in tap water
Motor Efficiency	85 percent
Minimum Basin D.O.	1 mg/l

Oxygen is monitored in the basins using D.O. probes.

Secondary Clarifiers

All secondary clarifiers are circular units. The side water depth is 3.0 meters (10 ft.) and the overflow rate is 500 gpd/sq. ft.). Sludge recycle pumps are sized to deliver 50 percent of the average flow.

Sludge Holding Tank-Thickener

For the smaller plants, a sludge-holding tank is provided, with sufficient capacity to hold 5 days flow from the aerobic digester. The thickener provided for the larger plants was designed on the basis of 29 kg/m^2/day (6 lbs./sq. ft./day) and a side water depth of 3.0 meters (10 ft.)

Aerobic Digester

The aerobic digester is sized on the basis of a hydraulic detention time of 20 days. The sizing of the aerator-mixers was based on 0.044HP/m^3 (1.25 HP/1,000 cu.ft.) of digester volume.

Vacuum Filtration

The vacuum filters were sized on cake yield of 9.75 kg/m^2/hr. (2 lbs./sq.ft./hr) and a maximum running time of 18 hrs./day. The polymer system was sized to deliver up to 0.005kg of polymer/kg of day solids (10 lbs. of polymer/ton dry solids).

Granular Media Filters

The filters are sized on the basis of an average hydraulic loading of 9.12m^3/m^2/min. (3 gpm/sq.ft.) Backwash facilities are sized to provide rate up to 0.82m^3/m^2/min. (20 gpm/sq.ft.) and a backwash cycle of up to 20 minutes duration.

Final Sludge Disposal

Sludge is disposed of at a sanitary landfill assumed to be 5 miles from the waste water treatment facility.

Design Philosophy

The plant's forward flow units are designed for parallel flow, i.e. either half of the plant can be operated independently. The sludge facilities are designed on the basis of series flow. All outside tankage is reinforced concrete. The tops of all outside tankage are assumed to be 12 ft above grade.

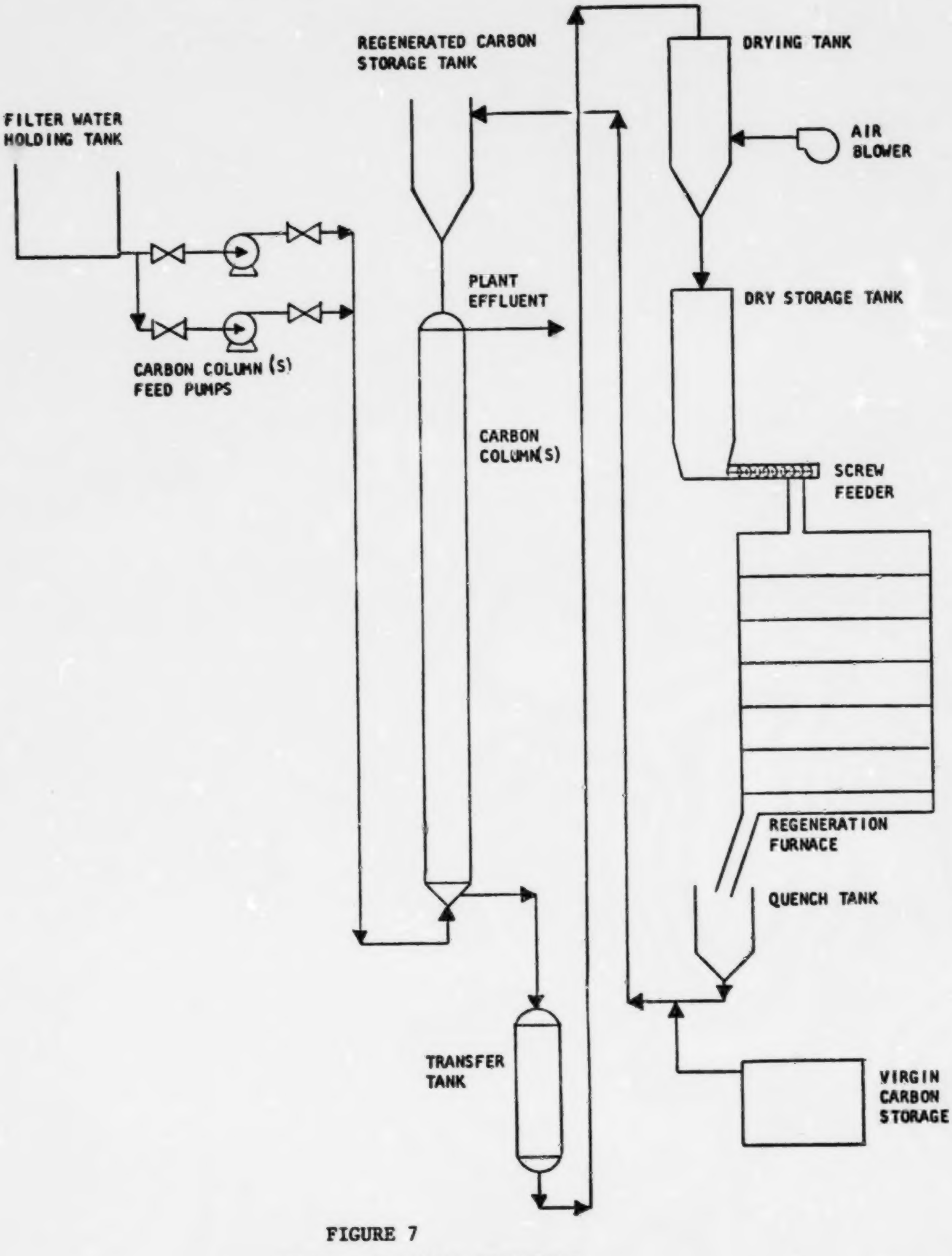

FIGURE 7

BATEA - PROPOSED TREATMENT

TABLE 47

BATEA - END OF PIPE TREATMENT SYSTEM
DESIGN SUMMARY

Granular Carbon Columns

The carbon columns are sized on a hydraulic loading of 0.4-0.8 $m^3/m^2/min.$ (10-20 gpm/sq. ft.) and a column detention time of 40 minutes. A backwash rate of (50 gpm/sq. ft.) was assumed for 40 percent bed expansion at 70°F.

Filter-Column Decant Sump

Tankage is provided to hold the backwash water and decant it back to the treatment plant over a 24-hour period. This will eliminate hydraulic surging of the treatment units.

Regeneration Furnace

An exhaustion rate of 1 kg of COD/kg carbon (1 lb COD/1b carbon) was used for sizing the regeneration facilities.

Regenerated Exhausted Carbon Storage

Tankage is provided to handle the regenerated and exhausted carbon both before and after regeneration.

Estimated Costs of Facilities

As discussed previously, designs for the model treatment systems were costed out in order to evaluate the economic impact of the proposed effluent limitations. The design considerations resulted in the generation of cost data which would be conservative. However, relatively conservative cost numbers are preferred for this type of general, economic analysis.

Activated sludge followed by granular media filtration was used as the BPCTCA treatment system. The plant designs were varied to generate cost effectiveness data within each category. Activated carbon adsorption was used as the BATEA treatment.

Capital and annual cost data were prepared for each of the proposed treatment systems.

The capital costs were generated on a unit process basis, e.g. equalization, neutralization, etc. for all the proposed treatment systems. The following "percent add on" figures were applied to the total unit process costs in order to develop the total capital cost requirements:

Item	Percent of Unit Process Capital Cost
Electrical	12
Piping	15
Instrumentation	8
Site work	3
Engineering Design and Construction Supervision Fees	15
Construction Contingency	15

Land costs were computed independently and added directly to the total capital costs.

Annual costs were computed using the following cost basis:

Item	Cost Allocation
Amortization	10 percent of investment.
Depreciation	5 year-straight line with zero salvage value.
Operations and Maintenance	Includes labor and supervision, chemicals sludge, hauling and disposal, insurance and taxes (computed at 2 percent of the capital cost), and maintenance (computed at 4 percent of the capital cost).
Power	Based on $1.50/100 KWH for electrical power.

The short term capitalization and depreciation write-off period is that which is presently acceptable under current Internal Revenue Service Regulations pertaining to industrial pollution control equipment.

All cost data were computed in terms of August, 1971 dollars, which corresponds to an Engineering News Records (ENR) value of 1580.

The following is a qualitative as well as a quantitative discussion of the possible effects that variations in treatment technology or design criteria could have on the total capital costs and annual costs.

Technology or Design Criteria	Capital Cost Differential
1. Use aerated lagoons and sludge dewatering lagoons in place of the proposed treatment system.	1. The cost reduction could be to 70 percent of the proposed figures.
2. Use earthern basins with a plastic liner in place of reinforced concrete construction, and floating aerators versus platform-mounted aerators with permanent-access walkways.	2. Cost reduction could be 10 to 15 percent of the total cost.
3. Place all treatment tankage above grade to minimize excavation, espcaially if a pumping station is required in any case. Use all-steel tankage to minize capital cost.	3. Cost savings would depend on the individual situation.
4. Minimize flow and maximize concentrations through extensive in-plant recovery and water conservation, so that other treatment technologies (e.g. incineration) may be economically competitive.	4. Cost differential would depend on a number of items, e.g. age of plant, accessibility to process piping, local air pollution standards, etc.

The following table summarizes the general ranges of sludge quantities generated by small, medium, and large refineries in each subcategory.

Subcategory	cu m/yr [1]	cu yd/yr [1]
Topping	2.3-15	3 - 20
Low Cracking	76-380	100 - 500
High Cracking	380-2300	500 - 3000
Petrochemical	460-3800	600 - 5000
Lube	610-6900	800 - 9000
Integrated	760-9200	1000 - 12000

[1] Wet-weight basis

Particular plants within the petrochemical, lube, and integrated subcategories may be amenable to sludge incineration because of the large quantities of sludge involved. For example, sludge incineration would reduce the previous quantities by about 90 percent. Sludge cake is 80 percent water, which is evaporated during incineration, and more than half of the remaining (20 percent) solids are thermally oxidized during incineration. Sludge incineration costs were not evaluated for those specific cases, because the particular economics depend to a large degree on the accessibility of a sanitary landfill and the relative associated hauling costs.

The following discussion is presented to help visualize the complexities involved in evaluating cost effectiveness data. Every treatment system is composed of units whose design basis is primarily hydraulically dependent, organically dependent, or a combination of the two. The following is a list of the unit processes employed, and a breakdown of the design basis.

Hydraulically Dependent	Organically Dependent	Hydraulically and Organically Dependent
Pump station	Thickener	Aeration basin
API separator	Aerobic Digestor	Oxygen transfer equipment
Equalization	Vacuum filter	Air flotation Unit
Neutralization		
Nutrient addition		
Sludge recycle pump		
Clarifier		

The annual cost associated with the hydraulically dependent unit processes is not a function of effluent level. On the other hand, the sizing of the organically dependent units should theoretically vary in direct proportion to the effluent level: e.g. reducing the BOD_5 removal from 95 to 85 percent should reduce the sizes of the sludge handling equipment by approximately 10 percent. However, there are two complicating factors: 1) only a relatively few sizes of commercially available equipment; and 2) broad capacity ranges. These two factors, especially in regard to vacuum filters, tend to negate differentials in capital cost with decreasing treatment levels.

The relationship between design varying contaminant levels and the design of aeration basins and oxygen transfer equipment is somewhat more complex. The levels are dependent on the hydraulic flow, organic concentration, sludge settleability, and the relationship between mixing and oxygen requirements. For example, to reach a particular effluent level, the waste water's organic removal kinetics will require a particular detention time at a given mixed-liquor concentration. The oxygen transfer capacity of the aerators may or may not be sufficient to keep the mixed liquor suspended solids in suspension within the aeration basin. Therefore, the required horsepower would be increased merely to fulfill a solids mixing requirement. Alternatively, the oxygen requirements may be such that the manufacturer's recommended minimum spacing and water depth requirements would require that the basin volume be increased to accommodate oxygen transfer requirements.

Non-Water Quality Aspects

The major nonwater quality consideration which may be associated with in-process control measures is the use of and alternative means of ultimate disposal of either liquid or solid wastes. As the process Raw Waste Load is reduced in volume, alternate disposal techniques such as incineration, ocean discharge, and deep-well injection are feasible. Recent regulations are tending to limit the applicability of ocean discharge and deep-well injection because of the potential long-term detrimental effects associated with these disposal procedures. Incineration may be a viable alternative for highly concentrated waste streams. However, associated air pollution and the need for auxiliary fuel, depending on the heating value of the waste, are considerations which must be evaluated on an individual basis for each use. Other nonwater quality aspects, such as noise levels, will not be perceptibly affected. Most refineries generate fairly high noise levels (85-95 dB(A)) within the battery limits because of equipment such as pumps, compressors, steam jets, flare stacks, etc. Equipment associated with in-process or end-of-pipe control systems would not add significantly to these levels. In some cases, substituting vacuum pumps for steam jets would in fact reduce plant noise levels. There are no radioactive nuclides used in the industry, other than in instrumentation. Thus no radiation problems will be expected. Compared to the odor emissions possible from other refinery sources, odors from the waste water treatment plants are not expected to create a significant problem. However, odors are possible from the waste water facilities, especially from the possible stripping of ammonia and sulfides in the air flotation units, and from accidental anaerobic conditions in biological facilities during upsets.

The extra power required for waste water treatment and control systems is negligible compared to the total power requirements of the petroleum refining equipment.

SECTION IX

BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE--EFFLUENT LIMITATIONS

Based on the information contained in Sections III through VIII of this report, effluent limitations commensurate with the best practicable control technology currently available have been established for each petroleum refining subcategory. The limitations, which explicitly set numerical values for the allowable pollutant discharges within each subcategory, are presented in Tables 1-6. The effluent limitations specify allowable discharges of BOD5, COD, TOC, total suspended solids, oil and grease, phenolic compounds, ammonia (N), sulfides, total and hexavalent chromium; based upon removals which are capable of being attained through the application of BPCTCA pollution control technology.

The best practicable control technology currently available is based on both in-plant and end-of-pipe technology. BPCTCA in-plant technology is based on control practices widely used within the petroleum refining industry, and include the following:

1. Installation of sour water strippers to reduce the sulfide and ammonia concentrations entering the treatment plant.

2. Elimination of once-through barometric condenser water by using surface condensers or recycle systems with oily water cooling towers.

3. Segregation of sewers, so that unpolluted storm runoff and once-through cooling waters are not treated normally with the process and other polluted waters.

4. Elimination of polluted once-through cooling water, by monitoring and repair of surface condensers or by use of wet and dry recycle systems.

BPCTCA end-of-pipe treatment technology is based on the existing waste water treatment processes currently used in the Petroleum Refining Industry. These consist of equalization and storm diversion; initial oil and solids removal (API separators or baffle plate separators); further oil and solids removal (clarifiers, dissolved air flotation, or filters); carbonaceous waste removal (activated sludge, aerated lagoons, oxidation ponds, trickling filter, activated carbon, or combinations of these); and filters (sand, dual media; or multi-media) following biological treatment methods. It must be recognized that specific treatability studies are required prior to the application of a specific treatment system to the individual refinery.

Granular media filtration or polishing ponds prior to final discharge are included so that the total suspended solids and oil

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concentrations in the final effluent can be generally maintained at approximately 10 mg/l and 5 mg/l, respectively. The final polishing step is considered BPCTCA for the petroleum refining industry since several refineries are now using polishing ponds, and granular media filters are becoming accepted technology with a few installations operating currently and several more now under construction.

In a petroleum refinery the waste water treatment plant should be used to treat only polluted waters. All once-through cooling water or storm runoff which is unpolluted should be segregated as it dilutes the polluted waters and requires treatment of a greater flow. Flows for BPCTCA were based on the 50 percent probability of occurance flows for plants practicing recycle with less than 3 percent heat removal by once-through cooling water (on a dry weather basis). Recognizing the additional flows and waste loads associated with rain runoff and ballast waters, allocations for these added flows must be given based on strict segregation of runoff and ballast waters treated.

PROCEDURE FOR DEVELOPMENT OF BPCTCA EFFLUENT LIMITATIONS

The effluent guideline limitations were determined using effluent data from refineries visited during this project or attainable effluent concentrations and the 50 percent probability of occurance flow from the refineries with 3 percent or less of the heat removed by once-through cooling water. In some cases the available data from the refineries visited was considered to be too stringent to be met by the industry in general. In these cases the flow and concentration procedure was used. The median flows are presented in Table 23, Section V. The attainable concentrations for BPCTCA are presented in Table 48. Refinery data are presented in Tables 26-28, Section VII.

Several exceptions to this procedure were required to establish meaningful effluent limitations in specific cases. These are as follows:

Topping, Cracking, Petrochemical, Lube, and Integrated Subcategories - Ammonia as Nitrogen

The ammonia as nitrogen effluent limitations were calculated using an 80 percent reduction from the 50 percent probability of occurance raw waste loads in each subcategory.

Topping, Cracking, Petrochemial, Lube and Integrated Subcategories - TOC

Little data is available on the reduction of TOC. Available effluent data indicate an effluent TOC/BOD ratio of less than 2.2. Using this factor, effluent limitations for TOC, were based on BOD_5 limitations. It is recognized that this ratio (TOC/BOD) is variable between the refineries, and prior to use, an agreed upon correlation should be developed for the individual refinery.

TABLE 48

Attainable Concentrations from the Application of Best Practicable Control Technology Currently Available

Parameter	Concentration mg/l
BOD5	15
COD	*
TOC	*(2.2 x BOD5)
SS	10
O & G	5
Phenol	0.1
NH3-N	*(80% removal)
Sulfide	0.1
CrT	.25
Cr6	.005

*See Text

Topping, Cracking, Petrochemical, Lube and Integrated Subcategories - COD

The COD effluent concentrations were determined from refinery effluent data and are as follows: topping - 80 mg/l; cracking - 115 mg/l; petrochemical - 96 mg/l; lube - 110 mg/l; and integrated - 110 mg/l.

The long term (annual or design) average effluent limitations determined are contained in Table 49.

Statistical Variability of a Properly Designed and Operated Waste Treatment Plant

The effluent from a properly designed and operated treatment plant changes continually due to a variety of factors. Changes in production mix, production rate and reaction chemistry influence the composition of raw wasteload and, therefore, its treatability. Changes in biological factors influence the efficiency of the treatment process. A common indicator of the pollution characteristics of the discharge from a plant is the long-term average of the effluent load, however, the long-term (e.g., design or yearly) average is not a suitable parameter on which to base an enforcement standard. However, using data which show the variability in the effluent load, statistical analyses can be used to compute short-term limits (30 day average or daily) which should never be exceeded, provided that the plant is designed and run in the proper way to achieve the desired long-term average load. It is these short-term limits on which make up the effluent guidelines.

In order to reflect the variabilities associated with properly designed and operated treatment plants for each of the parameters as discussed above, a statistical analysis was made of plants where sufficient data was available to determine these variances for day-to-day and month-to-month operations.

This data was acquired during the initial field investigation or submitted by API or other industry sources.

The variability data have been treated in the following manner:

a. The form of the statistical distribution which most generally describes the data for all plants was determined;

b. For each plant the statistical parameter which best fit the plants' data to the above distribution were calculated;

c. Values of "daily maximum" and "30 day maximum" variabilities were then determined using the values calculated above. The daily maximum variability was set embracing 99% of the expected variation and the 30 day average was set embracing 98% of the expected variation.

TABLE 49
BPCTCA

PETROLEUM REFINING INDUSTRY EFFLUENT LIMITATIONS

Annual Daily Kilograms of Pollutants/1000Cubic Meters Feedstock (1) Per Stream Day
(Annual Average Daily Pounds of Pollutant/1000 BBL of Feedstock Per Stream Day)

Refinery Subcategory	BOD5	COD	TOC	Total Suspended Solids	Oil & Grease	Phenolic Compounds	Ammonia(N)	Sulfide	Total Chromium	Hexavalent Chromium
Topping	7.1(2.5)	37.6(13.3)	15.6(5.5)	4.8(1.7)	2.3(0.83)	0.048(0.017)	0.85(0.30)	0.048(0.017)	0.119(0.042)	0.0023(0.0008)
Cracking	8.8(3.1)	67.9(24.0)	19.2(6.8)	5.9(2.1)	2.8(1.0)	0.059(0.021)	5.7 (2.0)	0.059(0.021)	0.147(0.052)	0.0028(0.0010)
Petrochemical	10.8(3.8)	67.9(24.0)	23.5(8.3)	7.1(2.5)	3.7(1.3)	0.071(0.025)	7.1 (2.5)	0.071(0.025)	0.178(0.063)	0.0037(0.0013)
Lube	15.8(5.6)	116 (41.0)	35.1(12.4)	10.8(3.8)	5.4(1.9)	0.108(0.038)	7.1 (2.5)	0.108(0.038)	).266(0.094)	0.0054(0.0019)
Integrated	17.0(6.0)	125 (44.0)	37.4(13.2)	11.3(4.0)	5.7(2.0)	0.113(0.040	7.1 (2.5)	0.113(0.040)	0.283(0.10)	0.0056(0.0020)
Runoff(2)	0.015(0.125)	0.12 (1.0)	0.033(0.275)	0.010(0.083)	0.0050(0.042)	--	--	--	--	--
Ballast(3)	0.015(0.125)	0.15(1.250)	0.033(0.275)	0.010(0.083)	0.0050(0.042)	--	--	--	--	--

(1) Feedstock - Crude oil and/or natural gas liquids.
(2) The additional allocation being allowed for contaminated storm runoff flow, kg/cubic meter (lb/1000 gallons), shall be based solely on that storm flow which passes through the treatment system. All additional storm runoff, that has been segregated from the main waste stream, shall not exceed a TOC concentration of 35 mg/l or Oil and Grease concentration of 15 mg/l when discharged.
(3) This is an additional allocation, based on ballast water intake - kilograms per 1000 liters (pounds per 1000 gallons).

Results of the Data analysis:

The data from each refinery were determined to be eiter normally or log normally distributed.

The daily maximums, when the data is normally distributed, the variability is equal to $\frac{x + 2.327\,Q;}{x}$ where x is the mean or design average and Q is the standard deviation for the data.

When the data was log normally distributed, the variability is equal to $10^{(4.65-2.30R)R/2}$: where R is the standard deviation of the logarithm of the data points.

The variability factors used are contained in Table 50. These factors for each parameter except total and hexavalent chromium were calculated from long-term refinery data. The factor for total chromium is the same as that used for suspended solids since metallic ion is removed as an insoluble salt. The variability factor for hexavalent chromium was based on the sulfide variability. The guidelines for BPCTCA presented in Tables 1-6 have taken into consideration the above variability factors.

Process and Size Factor

A complete process breakdown of many of the U.S. refineries is contained in Table 51. This table was prepared from the best published data available (Oil and Gas Journal, International Petroluem Encyclopedia, and the EPA/API Raw Waste Load Survey of 1972), but should only be used as a guide. The values used to determined the process and size factors for permit issuance should be documented by the individual refineries.

An example calculation of the process and size factors follows below. It should be noted that only crude processes, cracking processes, lube processes, and asphalt processes enter into the calculation of process configuration.

Process category	Processes included	Weighting factor
Crude	Atm. crude distillation Vacuum crude distillation. Desalting	1
Cracking and coking	Fluid cat. cracking Vis-breaking. Thermal cracking Moving bed cat. cracking Hydrocracking Fluid coking Delayed coking	6

TABLE 50

VARIABILITY FACTORS BASED ON PROPERLY DESIGNED AND OPERATED WASTE TREATMENT FACILITIES

	BOD5	COD	TOC	TSS	O & G	Phenol	Ammonia	Sulfide	CrT	Cr6
Daily Variability	3.2	3.1	3.1	2.9	3.0	3.5	3.3	3.1	2.9	3.1
30 Day Average Variability	1.7	1.6	1.6	1.7	1.6	1.7	1.5	1.4	1.7	1.4

Lube	Further defined in Table 51.	13
Asphalt	Asphalt production Asphalt oxidation Asphalt emulsifying	12

Example: Lube Refinery - 125,000 bbl/day stream day

Process	Capacity (1,000 bbl per stream day)	Capacity relative to throughput		Weighting factor		Process configuration
Crude - ATM	125	1				
Vacuum	60	.48				
Desalting	125	1				
Total		2.48	X	1	=	2.48
Cracking - FCC	41	.328				
Hydrocracking	20	.160				
Total		.488	X	6	=	2.48
Lubes						
Lube Hydrofining	5.3	.042				
Furfural Extraction	4.0	.032				
Phenol Extraction	4.0	.030				
Total		.113	X	13	=	1.47
Asphalt	4.0	0.032	X	12	=	.38
	Refinery process configuration				=	7.26

NOTES

See Table 4 for process factor. Process factor = 0.88. See Table 4 for size factor for 125,000 bbl per stream day lube refinery. Size factor = 0.93. To calculate the limits for each parameter, multiply the limit Table 4 by both the process factor and size factor. BOD5 limit (maximum for any 1 day) = 17.9 x 0.88 x 0.93=14.6 lb. per 1,000 bbl of feedstock.

TABLE 51

PETROLEUM REFINING - PROCESS BREAKDOWN

Legend:

A. Crude Processes

D - desalting
A - atmospheric distillation
V - vacuum distillation

B. Cracking Processes

FCC - fluid catalytic cracking
Thermo. - thermofor
Houdri. - houdriflow
Gas-Oil Cr.- gas-oil cracking
Visbreak. - visbreaking
Fl. Coke - fluid coking
Delay.Coke - delayed coking

C. Lube Processes

A - lube hydrofining
B - white oil manufacturing
C - propane - dewaxing, deasphalting
D - duo sol, solvent dewaxing
E - lube vac. tower, wax fract.
F - centrifuging and chilling
G - MEK dewaxing
H - deoiling (wax)
I - naphthenic lubes
J - SO2 extraction
k - wax pressing
L - wax plant (with neutral separ.)
M - furfural extraction
N - clay contacting - percolation
O - wax sweating
P - acid treating
Q - phenol extraction

TABLE 51 cont'd
PETROLEUM REFINERY - PROCESS BREAKDOWN

COMPANY	REGION	LOCATION	STATE	SUBCAT.	REFINERY CAPACITY 1000 bbl/day	CRUDE PROCESSES Process	CRUDE PROCESSES Capacity 1000 bbl/day	CRACKING PROCESSES Process	CRACKING PROCESSES Capacity 1000 bbl/day	LUBE PROCESSES Process	LUBE PROCESSES Capacity 1000 bbl/day	ASPHALT PRODUCTION Capacity 1000 bbl/day	PROCESS CONFIG-URATION
Amerada Hess Corporation	2	Port Reading	N.J.	B	75.0	D A V	75.0 75.0 30.0	FCC	45.0				6.00
Chevron Oil Company	2	Perth Amboy	N.J.	B	92.0	D A V	92.0 92.0 50.0	Houdri.	38.0			25.0	8.28
Exxon Co., USA	2	Linden	N.J.	C	286.0	D A V	286.0 286.0 143.0	FCC Visbreak.	140.0 2.2			46.0	7.41
Mobil Oil Corporation	2	Paulsboro	N.J.	D	100.5	D A V	100.5 100.5 62.6	Thermo. Delay. Cok.	25.0 23.7	Unk.	13.0		7.21
Texaco Inc.	2	Westville	N.J.	C	88.0	D A V	88.0 88.0 29.5	FCC Visbreak.	40.0 13.0				5.95
Ashland Petro. Company	2	Tonawanda	N.Y.	C	67.0	D A V	67.0 67.0 25.0	FCC	20.0			10.0	5.96
Amerada-Hess Corporation	2	St. Croix	V.I.	A	418.0	D A V	418.0 418.0 20.0						2.0
Caribbean Gulf Ref. Company	2	Bayamon	P.R.	B	40.0	D A V	40.0 40.0 9.0	FCC	8.5				3.50
Commonwealth Oil Refining Co. Inc.	2	Penuelas	P.R.	C	100.0	D A V	100.0 100.0 50.0	FCC Visbreak.	40.0 22.0				6.22
Yabocoa Sun Oil Company	2	Yabocoa	P.R.	A	66.0	D A V	66.0 66.0 30.0			E G M	5.0 8.5 6.0		6.30

TABLE 51 cont'd

PETROLEUM REFINERY - PROCESS BREAKDOWN

COMPANY	REGION	LOCATION	STATE	SUBCAT.	REFINERY CAPACITY 1000 bbl day	CRUDE PROCESSES Process	CRUDE PROCESSES Capacity 1000 bbl day	CRACKING PROCESSES Process	CRACKING PROCESSES Capacity 1000 bbl day	LUBE PROCESSES Process	LUBE PROCESSES Capacity 1000 bbl day	ASPHALT PRODUCTION Capacity 1000 bbl/day	PROCESS CONFIG-URATION
Getty Oil Co. Inc.	3	Delaware City	Del.	C	150.0	D A V	150.0 150.0 90.7	FCC Hydro. Fl. Coke	77.0 17.0 44.0				8.12
Amoco Oil Company	3	Baltimore	MD.	A	10.0	A	10.0					8.0	10.6
Chevron Asphalt Company	3	Baltimore	MD.	A	13.8	D A V	13.8 13.8 13.8					11.0	12.6
Atlantic Richfield Company	3	Phila.	PA.	B	195.0	D A V	195.0 195.0 57.0	Hydro.	30.0			19.5	4.42
BP Oil Corporation	3	Marcus Hook	PA.	B	105.0	D A V	105.0 105.0 60.0	FCC Visbreak.	41.9 12.0				5.65
Bradford Pet. (Witco)	3	Bradford	PA.	A	7.8	D A	7.8 7.8			Unk.	3.1		7.17
Gulf Oil Company	3	Phila.	PA.	B	174.0	D A V	174.0 174.0 65.0	FCC	80.5				5.15
Pennzoil Company	3	Rouseville	PA.	A	10.4	D A V	10.4 10.4 3.3			C D	0.7 3.0		6.94
Quaker State Oil Ref. Corporation	3	Emlenton	PA.	A	3.5	D A V	3.5 3.5 1.7			Unk.	3.0		13.63
Quaker State Oil Ref. Corporation	3	Farmers Valley	PA.	A	6.8	D A V	6.8 6.8 2.75			C G M	1.0 2.5 2.0		12.92
Sun Oil Company	3	Marcus Hook	PA.	E	180.0	D A V	180.0 180.0 48.0	FCC	85.0	D E G I M	5.8 11.7 13.4 10.7 4.0	12.0	9.19
United Refining Company	3	Warren	PA.	B	38.0	D A V	38.0 38.0 8.0	FCC	10.2			4.0	5.08

TABLE 51 cont'd

PETROLEUM REFINERY - PROCESS BREAKDOWN

COMPANY	REGION	LOCATION	STATE	SUBCAT.	REFINERY CAPACITY 1000 bbl/day	CRUDE PROCESSES Process	CRUDE PROCESSES Capacity 1000 bbl/day	CRACKING PROCESSES Process	CRACKING PROCESSES Capacity 1000 bbl/day	LUBE PROCESSES Process	LUBE PROCESSES Capacity 1000 bbl/day	ASPHALT PRODUCTION Capacity 1000 bbl/day	PROCESS CONFIGURATION
Valvoline Oil Company	3	Freedom	PA.	A	6.5	D A V	6.5 6.5 2.0			Unk.	1.3		4.91
Wolf's Head Oil (Pennzoil)	3	Reno	PA.	A	2.22	A	2.22			F K	0.95 0.6		10.08
Amoco Oil Company	3	Yorktown	VA.	C	53.0	D A V	53.0 53.0 28.0	FCC Delay. Coke	30.5 14.0				7.57
Pennzoil Company	3	Falling Rock	W.V.	A	5.5	D A V	5.5 5.5 2.5			F K	2.4 1.0		10.49
Quaker State Oil Ref. Corporation	3	Newell	W.V.	A	10.0	D A V	10.0 10.0 4.0			Unk.	7.0		11.50
Quaker State Oil Ref. Corporation	3	St. Mary's	W.V.	A	5.0	D A V	5.0 5.0 2.2			C F K M	0.7 1.85 1.25 0.8		14.40
Hunt Oil Co.	4	Tuscaloosa	ALA.	A	15.75	D A V	15.75 15.75 8.66					5.2	6.51
Marion Corp.	4	Mobile	ALA.	A	15.5	D A	15.5 15.5						2.0
Vulcan Asphalt Refining Co.	4	Cordova	ALA.	A	3.0	A	3.0					1.8	8.20
Warrior Asphalt Corp.	4	Holt	ALA.	A	2.6	A	2.6					1.73	8.98
Seminole Asphalt Refining, Inc.	4	St. Mark's	FLA.	A	5.5	D A V	5.5 5.5 2.4					2.5	7.89
Amoco Oil Co.	4	Savannah	GA.	A	12.0	A	12.0					5.5	6.5
Young Refining Corp.	4	Douglasville	GA.	A	2.5	A	2.5						

TABLE 51 cont'd
PETROLEUM REFINERY - PROCESS BREAKDOWN

COMPANY	REGION	LOCATION	STATE	SUBCAT.	REFINERY CAPACITY 1000 bbl/day	CRUDE PROCESSES		CRACKING PROCESSES		LUBE PROCESSES		ASPHALT PRODUCTION Capacity 1000 bbl/day	PROCESS CONFIG-URATION
						Process	Capacity 1000 bbl/day	Process	Capacity 1000 bbl/day	Process	Capacity 1000 bbl/day		
Ashland Oil, Inc.	4	Catlettsburg	KY.	C	138.0	D A V	138.0 138.0 55.0	FCC Visbreak.	55.0 4.0			10.0	5.83
Ashland Oil, Inc.	4	Louisville	KY.	B	26.0	D A V	26.0 26.0 10.0	FCC	9.0			3.5	6.08
Somerset Refining Inc.	4	Somerset	KY.	A	3.0	A	3.0					2.5	11.00
Amerada Hess Corporation	4	Purvis	MISS.	B	30.0	D A	30.0 30.0	Thermo. Delay coke Hydro.	30.5 6.7 3.0				10.04
Southland Oil Company	4	Crupp	MISS.	A	3.2	D A	3.2 3.2					1.44	7.40
Southland Oil Company	4	Lumberton	MISS.	A	4.26	D A	4.26 4.26					2.35	8.62
Southland Oil Company	4	Sandersville	MISS.	A	8.3	D A V	8.3 8.3 4.6					3.5	7.61
STD. Oil of Kentucky	4	Pascagoula	KY.	C	240.0	D A V	240.0 240.0 148.0	FCC Hydro.	58.0 59.0				5.54
Delta Refining Company	4	Memphis	TENN.	B	30.0	D A	30.0 30.0	Thermo.	12.0			3.0	5.60
Amoco Oil Company	5	WoodRiver	ILL.	C	107.0	D A V	107.0 107.0 40.0	FCC	42.0			10.8	5.94
Clark Oil and Refining Corp.	5	Blue Island	ILL.	C	70.0	D A V	70.0 70.0 27.0	FCC Hydro.	25.0 11.0			4.5	6.24
Clark Oil and Refining Corp.	5	Hartford	ILL.	B	38.0	D A V	38.0 38.0 15.0	FCC Delay. coke	27.0 13.0				8.71
Marathon Oil Company	5	Robinson	ILL.	B	205.0	D A	205.0 205.0	Gas-Oil Cr. Delay.	2.8 19.0				4.89

TABLE 51 cont'd
PETROLEUM REFINERY - PROCESS BREAKDOWN

COMPANY	REGION	LOCATION	STATE	SUBCAT.	REFINERY CAPACITY 1000 bbl/day	CRUDE PROCESSES Process	CRUDE PROCESSES Capacity 1000 bbl/day	CRACKING PROCESSES Process	CRACKING PROCESSES Capacity 1000 bbl/day	LUBE PROCESSES Process	LUBE PROCESSES Capacity 1000 bbl/day	ASPHALT PRODUCTION Capacity 1000 bbl/day	PROCESS CONFIGURATION
Mobil Oil Corporation	5	Joliet	ILL.	B	186.0	D A V	186.0 186.0 82.0	Delay. coke FCC	28.0 66.0				5.47
Shell Oil Company	5	Wood River	ILL.	D	268.0	D A V	268.0 268.0 91.5	Visbreak. FCC Hydro.	21.0 98.0 33.5	A C Q	5.6 11.2 5.6	22.5	7.85
Texaco Inc.	5	Lawrenceville	ILL.	B	84.0	D A V	84.0 84.0 24.0	Gas-Oil Cr. FCC	9.0 31.0			2.7	5.53
Texaco Inc.	5	Lockport	ILL.	B	72.0	D A V	72.0 72.0 14.0	Delay.Coke FCC	27.0 30.0				6.94
Union Oil Co. of California	5	Lemont	ILL.	B	152.0	D A V	152.0 152.0 55.0	Delay.Coke FCC	19.5 60.0			2.0	5.66
Wireback Oil Company	5	Plymouth	ILL.	A	1.5	A	1.5						1.0
Yetter Oil Company	5	Colmar	ILL.	A	1.0	D A V	1.0 1.0 1.0						3.0
Amoco Oil	5	Whiting	IND.	D	315.0	D A V	315.0 315.0 140.0	Delay.Coke FCC	14.5 146.0	A B C E G N Q	2.5 1.0 3.6 19.1 2.0 0.7 12.2	31.0	8.38
Atlantic Richfield Company	5	East Chicago	IND.	B	140.0	D A V	140.0 140.0 7.0	FCC	50.0			10.4	5.08
Gladieux Refinery Inc.	5	Port Wayne	IND.	A	10.0	D A	10.0 10.0						2.0
Ind. Farm Bureau Coop. Assoc. Inc.	5	Mt. Vernon	IND.	B	15.2	D A V	15.2 15.2 6.0	FCC	5.8				4.68
Laketon Asphalt Refinery Inc.	5	Laketun	IND.	A	8.5	D A V	8.5 8.5 5.0					2.6	6.26

TABLE 51 cont'd
PETROLEUM REFINERY - PROCESS BREAKDOWN

COMPANY	REGION	LOCATION	STATE	SUBCAT.	REFINERY CAPACITY 1000 bbl/day	CRUDE PROCESSES Process	CRUDE PROCESSES Capacity 1000 bbl/day	CRACKING PROCESSES Process	CRACKING PROCESSES Capacity 1000 bbl/day	LUBE PROCESSES Process	LUBE PROCESSES Capacity 1000 bbl/day	ASPHALT PRODUCTION Capacity 1000 bbl/day	PROCESS CONFIGURATION
Gulf Oil Company	5	Cleves	OH.	B	43.5	D A V	43.5 43.5 13.0	FCC	27.0			2.9	6.82
Gulf Oil Company	5	Toledo	OH.	B	51.0	D A V	51.0 51.0 12.5	FCC	22.0			2.0	5.30
STD. Oil Company of Ohio	5	Lima	OH.	D	175.0	D A V	175.0 175.0 51.0	Delay.Coke FCC Hydro.	15.0 45.5 20.0	G M	1.7 5.2		5.56
STD. Oio Company of Ohio	5	Toledo	OH.	B	125.0	D A V	125.0 125.0 43.0	Delay.Coke FCC Hydro.	12.8 71.5 36.0			7.0	8.79
Sun Oil	5	Toledo	OH.	C	130.0	D A V	130.0 130.0 22.0	FCC Hydro.	57.5 26.0				6.02
Murphy Oil Corporation	5	Superior	WIS.	B	38.0	D A V	38.0 38.0 15.5	FCC	10.7			12.0	7.89
Berry Petroleum Co.	6	Stephens	ARK.	A	3.5	D A V	3.5 3.5 1.0					1.0	5.71
Cross Oil and Refining Company	6	Smackover	ARK.	A	5.0	D A V	5.0 5.0 2.0			A	1.3	1.4	9.14
Lion Oil Company	6	El Dorado	ARK.	D	45.0	D A V	45.0 45.0 18.0	Solvent FCC Thermo.	5.0 12.5 7.7	unknown	0.8	6.0	7.58
MacMillian Ring-Free Oil Co., Inc.	6	Norphlet	ARK.	A	4.5	D A V	4.5 4.5 2.8					1.25	5.96
Atlas Processing Company	6	Shreveport	LA.	A	29.0	D A V	29.0 29.0 0.6						2.02

TABLE 51 cont'd
PETROLEUM REFINERY - PROCESS BREAKDOWN

COMPANY	REGION	LOCATION	STATE	SUBCAT.	REFINERY CAPACITY 1000 bbl/day	CRUDE PROCESSES		CRACKING PROCESSES		LUBE PROCESSES		ASPHALT PRODUCTION Capacity 1000 bbl/day	PROCESS CONFIG-URATION
						Process	Capacity 1000 bbl/day	Process	Capacity 1000 bbl/day	Process	Capacity 1000 bbl/day		
Gulf Oil Company	6	Belle Chase	LA.	B	186.0	D A V	186.0 186.0 55.0	Delay. Cok. FCC	16.0 78.0				5.33
Gulf Oil Company	6	Venice	LA.	B	29.1	D A	29.1 29.1	Hydro.	11.5				4.37
Kerr McGee Corporation	6	Cotton Valley	LA.	A	8.0	D A	8.0 8.0						2.0
LaJet Inc.	6	St. James	LA.	A	11.0	D A	11.0 11.0						2.0
Murphy Oil Corporation	6	Meraux	LA.	B	95.4	D A V	95.4 95.4 14.5	FCC	11.0				2.84
Shell Oil Company	6	Norco	LA.	B	250.0	D A V	250.0 250.0 90.0	Delay. Cok. FCC Hydro.	18.0 97.0 28.0			6.0	6.08
Tenneco Oil Company	6	Chalmette	LA.	B	97.0	D A V	97.0 97.0 23.0	Delay. Cok. FCC Hydro.	9.0 22.0 18.0				5.27
Texaco Inc.	6	Convent	LA.	B	140.0	D A V	140.0 140.0 35.0	Visbreak. FCC	12.0 70.0				5.76
Caribou Four Corners Inc.	6	Kirtland	N.M.	A	1.4	A	1.4						1.0
Famariss Oil Corporation	6	Monument	N.M.	A	5.0	A	5.0						1.0
Navajo Ref. Company	6	Artesia	N.M.	B	20.93	D A V	20.93 20.93 4.5	Gas-Oil Cr. Thermo.	1.25 5.2			1.4	4.87
Plateau Inc.	6	Bloomfield	N.M.	A	5.2	A	5.2						1.0
Shell Oil Company	6	Ciniza	N.M.	B	21.0	D A V	21.0 21.0 8.0	FCC	10.5			0.84	5.86
Thriftway Company	6	Bloomfield	N.M.	A	2.13	A	2.13						1.0
Allied Materials Corporation	6	Stroud	Okla.	A	5.8	D A V	5.8 5.8 2.8			Unk.	0.9	1.21	7.00

TABLE 51 cont'd
PETROLEUM REFINERY - PROCESS BREAKDOWN

COMPANY	REGION	LOCATION	STATE	SUBCAT.	REFINERY CAPACITY 1000 bbl/day	CRUDE PROCESSES Process	CRUDE PROCESSES Capacity 1000 bbl/day	CRACKING PROCESSES Process	CRACKING PROCESSES Capacity 1000 bbl/day	LUBE PROCESSES Process	LUBE PROCESSES Capacity 1000 bbl/day	ASPHALT PRODUCTION Capacity 1000 bbl/day	PROCESS CONFIG-URATION
Apco Oil Corporation	6	Cyril	Okla.	B	12.5	D A V	12.5 12.5 5.0	FCC	7.5			1.3	7.25
Champlin Petroleum Company	6	Enid	Okla.	D	52.0	D A V	52.0 52.0 18.0	Delay. Cok. FCC	3.7 21.45	D E F	3.1 1.0 1.6	1.4	7.02
Continental Oil Comapny	6	Ponca	Okla.	D	120.0	D A V	120.0 120.0 34.5	Gas-Oil Cr. Delay. Cok. FCC	13.5 18.5 44.6	D G M	2.1 2.2 1.9	3.0	7.09
Kerr-McGee Corporation	6	Wynnewood	Okla.	B	34.0	D A V	34.0 34.0 10.0	FCC Hydro.	13.5 4.5			3.5	6.71
Midland Coop. Inc.	6	Cushing	Okla	B	19.8	D A V	19.8 19.8 7.0	Delay. Cok. FCC	4.0 10.0				6.60
Okc Refining Inc.	6	Okmulgee	Okla	B	21.5	D A V	21.5 21.5 3.2	Thermo.	10.0			1.4	5.72
Sun Oil Company	6	Duncan	Okla.	B	50.0	D A V	50.0 50.0 17.0	Delay. Cok. FCC	12.0 35.5				8.04
Sun Oil Company	6	Tulsa	Okla.	D	90.0	D A V	90.0 90.0 31.5	Delay. Cok. FCC	8.2 31.4	C G M	8.2 8.0 13.6	4.2	9.85
Texaco Inc.	6	West Tulsa	Okla.	B	50.0	D A V	50.0 50.0 14.5	Gas-Oil Cr. FCC	6.0 18.0				5.17
Tonkawa Ref. Company	6	Tonkawa	Okla.	A	6.0	D A	6.0 6.0						2.0
Vickers Petro. Corporation	6	Ardmore	Okla.	B	32.0	D A V	32.0 32.0 11.0	Pitch FCC	2.5 13.0			5.0	7.13
Adobe Ref. Company	6	LaBlanca	Tex.	A	5.0	D A	5.0 5.0						2.0
American .Petrofina Inc.	6	Mt. Pleasant	Tex.	B	26.0	D A V	26.0 26.0 15.0	Thermo.	11.8			8.0	8.99

TABLE 51 cont'd
PETROLEUM REFINERY - PROCESS BREAKDOWN

COMPANY	REGION	LOCATION	STATE	SUBCAT.	REFINERY CAPACITY 1000 bbl/day	CRUDE PROCESSES Process	CRUDE PROCESSES Capacity 1000 bbl/day	CRACKING PROCESSES Process	CRACKING PROCESSES Capacity 1000 bbl/day	LUBE PROCESSES Process	LUBE PROCESSES Capacity 1000 bbl/day	ASPHALT PRODUCTION Capacity 1000 bbl/day	PROCESS CONFIGURATION
Apco Oil Corporation	6	Cyril	Okla.	B	12.5	D A V	12.5 12.5 5.0	FCC	7.5			1.3	7.25
Champlin Petroleum Company	6	Enid	Okla.	D	52.0	D A V	52.0 52.0 18.0	Delay. Cok. FCC	3.7 21.45	D E F	3.1 1.0 1.6	1.4	7.02
Continental Oil Comapny	6	Ponca	Okla.	D	120.0	D A V	120.0 120.0 34.5	Gas-Oil Cr. Delay. Cok. FCC	13.5 18.5 44.6	D G M	2.1 2.2 1.9	3.0	7.09
Kerr-McGee Corporation	6	Wynnewood	Okla.	B	34.0	D A V	34.0 34.0 10.0	FCC Hydro.	13.5 4.5			3.5	6.71
Midland Coop. Inc.	6	Cushing	Okla	B	19.8	D A V	19.8 19.8 7.0	Delay. Cok. FCC	4.0 10.0				6.60
Okc Refining Inc.	6	Okmulgee	Okla	B	21.5	D A V	21.5 21.5 3.2	Thermo.	10.0			1.4	5.72
Sun Oil Company	6	Duncan	Okla.	B	50.0	D A V	50.0 50.0 17.0	Delay. Cok. FCC	12.0 35.5				8.04
Sun Oil Company	6	Tulsa	Okla.	D	90.0	D A V	90.0 90.0 31.5	Delay. Cok. FCC	8.2 31.4	C G M	8.2 8.0 13.6	4.2	9.85
Texaco Inc.	6	West Tulsa	Okla.	B	50.0	D A V	50.0 50.0 14.5	Gas-Oil Cr. FCC	6.0 18.0				5.17
Tonkawa Ref. Company	6	Tonkawa	Okla.	A	6.0	D A	6.0 6.0						2.0
Vickers Petro. Corporation	6	Ardmore	Okla.	B	32.0	D A V	32.0 32.0 11.0	Pitch FCC	2.5 13.0			5.0	7.13
Adobe Ref. Company	6	LaBlanca	Tex.	A	5.0	D A	5.0 5.0						2.0
American Petrofina Inc.	6	Mt. Pleasant	Tex.	B	26.0	D A V	26.0 26.0 15.0	Thermo.	11.8			8.0	8.99

TABLE 51 cont'd
PETROLEUM REFINERY - PROCESS BREAKDOWN

COMPANY	REGION	LOCATION	STATE	SUBCAT.	REFINERY CAPACITY 1000 bbl day	CRUDE PROCESSES		CRACKING PROCESSES		LUBE PROCESSES		ASPHALT PRODUCTION Capacity 1000 bbl/day	PROCESS CONFIG-URATION
						Process	Capacity 1000 bbl day	Process	Capacity 1000 bbl day	Process	Capacity 1000 bbl day		
American Petrofina Inc.	6	Port Arthur	Tex.	B	84.0	D A V	84.0 84.0 28.0	Visbreak FCC	10.0 28.0				5.05
Amoco Oil Company	6	Texas City	Tex.	C	333.0	D A V	333.0 333.0 131.0	Delay. Cok. FCC Hydro.	22.5 185.0 38.0			5.3	7.01
Atlantic Richfield Company	6	Houston	Tex.	E	233.5	D A V	233.5 233.5 70.0	Delay. Cok. FCC Hydro.	27.0 74.0 4.5	A C D G Q	5.2 3.4 0.6 4.0 6.2		6.09
Champlin Petro. Company	6	Corpus Christi	Tex	B	63.0	A V	63.0 9.2	FCC	10.1				2.11
Charter Inter. Oil Company	6	Houston	Tex.	B	66.0	D A V	66.0 66.0 22.0	Visbreak. FCC	10.0 29.0			4.0	6.61
Coastal States Petrochemical Company	6	Corpus Christi	Tex.	C	135.0	D A V	135.0 135.0 33.0	Delay. Cok. FCC	12.0 19.3			0.5	3.68
Cosden Oil & Chemical Company	6	Big Spring	Tex.	C	65.0	D A V	65.0 65.0 25.0	Gas-Oil Cr. FCC	10.0 25.0			8.0	7.09
Crown Central Petro. Corp.	6	Houston	Tex.	B	103.0	D A V	103.0 103.0 38.0	Delay. Cok. FCC	9.5 52.0				5.95
Diamond Shamrock Oil & Gas Company	6	Sunray	Tex.	B	49.0	D A V	49.0 49.0 14.5	Gas-Oil Cr. Thermo. Houdri.	2.5 13.5 13.5			2.5	6.52
Eddy Ref. Company	6	Houston	Tex.	A	3.25	A	3.25						1.0
Exxon Company, USA	6	Baytown	Tex.	E	420.0	D A V	420.0 420.0 180.0	FCC Hydro.	145.0 20.0	C G Q	13.0 9.0 24.0	12.0	6.55
Flint Chemical Company	6	San Antonio	Tex.	A	0.75	A	0.75						1.0
Gulf Oil Company	6	Port Arthur	Tex.	E	319.0	D A V	319.0 319.0 147.4	Delay. Cok. FCC Hydro.	30.0 126.0 15.0	A C D	14.2 4.9 25.9		7.56

TABLE 51 cont'd
PETROLEUM REFINERY - PROCESS BREAKDOWN

COMPANY	REGION	LOCATION	STATE	SUBCAT.	REFINERY CAPACITY 1000 bbl day	CRUDE PROCESSES Process	CRUDE PROCESSES Capacity 1000 bbl day	CRACKING PROCESSES Process	CRACKING PROCESSES Capacity 1000 bbl day	LUBE PROCESSES Process	LUBE PROCESSES Capacity 1000 bbl day	ASPHALT PRODUCTION Capacity 1000 bbl/day	PROCESS CONFIG-URATION
Howell Hydrocarbon	6	San Antonio	TEX.	A	3.1	D A	3.1 3.1						2.0
La Gloria Oil and Gas Co.	6	Tyler	TEX.	B	29.0	D A	29.0 29.0	Gas-Oil Cr. Delay.Coke FCC	3.0 12.0 15.0				8.21
Longview Refining Company	6	Longview	TEX.	A	7.5	A	7.5						1.0
Marathon Oil Company	6	Texas City	TEX.	C	63.0	D A V	63.0 63.0 20.0	FCC	33.0				5.46
Mobil Oil Corporation	6	Beaumont	TEX.	D	335.0	D A V	335.0 335.0 103.0	Delay.Coke FCC Thermo. Hydro.	33.0 55.0 52.0 29.0	D G M	2.5 15.7 13.2	0.1	6.55
Phillips Petroleum Company	6	Borger	TEX.	C	95.0	D A	95.0 95.0	FCC	70.0				6.42
Phillips Petroleum Company	6	Sweeny	Tex.	C	85.0	D A V	85.0 85.0 17.0	FCC	35.0				4.67
Pride Ref. Inc.	6	Abilene	Tex.	A	14.69	D A	14.69 14.69						2.0
Quintana - Howell	6	Corpus Christi	Tex.	A	10.0	D A	10.0 10.0						2.0
Shell Oil Company	6	Deer Park	Tex.	D	293.0	D A V	293.0 293.0 106.4	Thermal Gas-Oil Cr. FCC Hydro.	20.0 65.0 70.0 25.0	A C G Q	8.0 3.3 7.9 6.8	3.8	7.36
Shell Oil Company	6	Odessa	Tex.	B	34.0	D A V	34.0 34.0 10.0	FCC	15.5				5.03
Southwestern Oil & Ref. Company	6	Corpus Christi	Tex.	B	150.0	D A V	150.0 150.0 24.0	FCC	12.0				2.64

TABLE 51 cont'd
PETROLEUM REFINERY - PROCESS BREAKDOWN

COMPANY	REGION	LOCATION	STATE	SUBCAT.	REFINERY CAPACITY 1000 bbl/day	CRUDE PROCESSES Process	CRUDE PROCESSES Capacity 1000 bbl/day	CRACKING PROCESSES Process	CRACKING PROCESSES Capacity 1000 bbl/day	LUBE PROCESSES Process	LUBE PROCESSES Capacity 1000 bbl/day	ASPHALT PRODUCTION Capacity 1000 bbl/day	PROCESS CONFIG-URATION
Suntide Refining Company	6	Corpus Christi	TEX.	C	60.0	D A V	60.0 60.0 10.0	Delay.Coke FCC	7.7 26.5				5.59
Tesoro Petro. Company	6	Carrizo Springs	TEX.	A	13.5	D A	13.5 13.5						2.0
Texaco,Inc.	6	Amarillo	TEX.	B	20.0	D A	20.0 20.0	Delay.Coke FCC	4.0 8.0				5.60
Texaco,Inc.	6	El Paso	TEX.	B	17.0	D A	17.0 17.0	Delay.Coke FCC	4.0 7.0				5.88
Texaco,Inc.	6	Port Arthur	TEX.	D	406.0	D A V	406.0 406.0 142.0	Gas-Oil Cr. FCC Hydro.	51.0 135.0 15.0	C G J M P	4.2 17.2 0.6 21.5 3.8		6.84
Texaco, Inc.	6	Port Neches	TEX.	A	47.0	D A V	28.0 47.0 26.0					9.0	4.45
Texas Asphalt and Refining Co.	6	Fort Worth	TEX.	A	3.5	A	3.5						1.0
Texas City Refining, Inc.	6	Texas City	TEX.	B	63.0	D A V	63.0 63.0 14.5	Visbreak. Houdri.	5.0 23.0				4.90
Three Rivers Refinery	6	Three Rivers	TEX.	A	1.5	A V	1.5 0.8			unknown	0.8	0.12	9.43
Union Oil Company of California	6	Nederland	TEX.	E	116.0	D A V	116.0 116.0 44.0	FCC	40.7	unknown	3.5	5.4	5.44
Union Texas Petro. (Allied)	6	Winnie	TEX.	B	10.0	A	10.0	Hydro.	3.0				2.8
Winston Refining	6	Fort Worth	TEX.	B	15.5	D A V	15.5 15.5 3.5	FCC	6.0				4.55

TABLE 51 cont'd
PETROLEUM REFINERY - PROCESS BREAKDOWN

COMPANY	REGION	LOCATION	STATE	SUBCAT.	REFINERY CAPACITY 1000 bbl/day	CRUDE PROCESSES		CRACKING PROCESSES		LUBE PROCESSES		ASPHALT PRODUCTION Capacity 1000 bbl/day	PROCESS CONFIG-URATION
						Process	Capacity 1000 bbl/day	Process	Capacity 1000 bbl/day	Process	Capacity 1000 bbl/day		
American Petrofina, Inc.	7	El Dorado	KAN.	B	25.0	D A V	25.0 25.0 9.0	FCC	11.5			2.0	6.08
Apco Oil Corporation	7	Arkansas City	KAN.	B	26.0	D A V	26.0 26.0 5.0	FCC Hydro.	12.0 2.95			1.4	6.29
CRA Inc.	7	Coffeyville	Kan.	D	36.0	D A V	36.0 36.0 12.5	Delay. Cok. FCC	8.5 14.2	G K M N	1.66 0.15 2.76 0.85		8.09
CRA Inc.	7	Phillipsburg	Kan.	B	21.0	D A V	21.0 21.0 7.5	FCC	7.35			2.0	5.60
Derby Ref. Company	7	Wichita	Kan.	B	27.0	D A V	27.0 27.0 8.8	Delay. Cok. Thermo.	3.8 12.55				5.96
Mid America Ref. Company Inc.	7	Chanute	Kan.	A	3.3	A V	3.3 1.8						1.55
Mobil Oil Corporation	7	Augusta	Kan.	B	52.0	A V	52.0 17.7	Gas-Oil Cr. Thermo.	4.1 23.5			8.0	6.37
National Coop. Ref. Assoc.	7	McPherson	Kan.	B	57.0	D A	57.0 57.0	Delay. Cok. FCC	17.0 21.0				6.0
North American Petro. Corp.	7	Shallow Water	Kan.	B	5.0	D A V	5.0 5.0 2.5	Thermo.	4.5				7.9
Phillips Petroleum Co.	7	Kansas City	KAN.	E	85.0	D A V	85.0 85.0 15.0	FCC	48.0	C E Q	5.2 6.8 2.4	3.0	8.19
Skelly Oil Company	7	El Dorado	KAN.	C	75.0	D A V	75.0 75.0 23.0	Delay.Coke FCC	9.8 48.0				6.93
Amoco Oil	[illegible]	Sugar Creek	KAN.	B	105.0	D A V	105.0 105.0 40.0	Delay.Coke FCC	11.0 50.0			6.5	6.61
Gary Western Co. (Gilsonite)	8	Grand Junction	COLO.	B	8.5	D A	8.5 8.5	Fluid.Coke	8.5				8.00

TABLE 51 cont'd

PETROLEUM REFINERY - PROCESS BREAKDOWN

COMPANY	REGION	LOCATION	STATE	SUBCAT.	REFINERY CAPACITY 1000 bbl/day	CRUDE PROCESSES		CRACKING PROCESSES		LUBE PROCESSES		ASPHALT PRODUCTION Capacity 1000 bbl/day	PROCESS CONFIG-URATION
						Process	Capacity 1000 bbl/day	Process	Capacity 1000 bbl/day	Process	Capacity 1000 bbl/day		
Continental Oil Company	8	Commerce City	COLO.	B	31.0	D A V	26.0 31.0 7.0	FCC	14.5			3.3	6.15
The Refinery Corporation	8	Commerce City	COLO.	B	17.5	D A V	17.5 17.5 3.5	Visbreak. FCC	6.0 6.5				6.49
Big West Oil Company	8	Kevin	MONT.	B	5.5	D A V	5.5 5.5 0.75	Gas-Oil Cr.	1.2			0.325	4.15
Cenex	8	Laurel	Mont.	B	44.0	D A V	44.0 44.0 15.4	FCC	18.0				4.81
Continental Oil Company	8	Billings	Mont.	B	56.0	D A V	38.0 56.0 12.2	FCC	21.0			3.5	4.90
Exxon Company USA	8	Billings	Mont.	B	46.0	D A V	46.0 46.0 18.0	Fluid. Cok. FCC Hydro.	5.2 34.0 4.9			13.0	11.54
Jet Fuel Refinery	8	Mosby	Mont.	A	1.0	A	1.0						1.0
Phillips Petro. Company	8	Great Falls	Mont.	B	5.7	D A V	5.7 5.7 2.0	FCC	3.0			0.8	7.19
Tesoro Petro. Corporation	8	Wolf Point	Mont.	A	2.65	A	2.65						1.0
Westco Ref. Company	8	Cut Bank	Mont.	B	5.0	D A	5.0 5.0	Gas-Oil Cr.	2.2				4.64
Amoco Oil Company	8	Mandan	N.D.	B	48.0	D A	48.0 48.0	FCC	34.0				6.25
Westland Oil Company	8	Williston	N.D.	B	5.0	D A	5.0 5.0	Gas-Oil Cr.	1.1				3.32
Amoco Oil Company	8	Salt Lake City	Utah	B	39.0	D A	39.0 39.0	FCC	22.0			2.5	6.15
Arizona Fuels Corporation	8	Roosevelt	Utah	B	11.0	D A	11.0 11.0	FCC	6.0				5.27
Caribou Four Corners Inc.	8	Woods Cross	Utah	B	5.0	D A V	5.0 5.0 1.0	Hydro.	1.0				3.4

TABLE 51 cont'd

PETROLEUM REFINERY - PROCESS BREAKDOWN

COMPANY	REGION	LOCATION	STATE	SUBCAT.	REFINERY CAPACITY 1000 bbl/day	CRUDE PROCESSES Process	CRUDE PROCESSES Capacity 1000 bbl/day	CRACKING PROCESSES Process	CRACKING PROCESSES Capacity 1000 bbl/day	LUBE PROCESSES Process	LUBE PROCESSES Capacity 1000 bbl/day	ASPHALT PRODUCTION Capacity 1000 bbl/day	PROCESS CONFIG-URATION
Chevron Oil Company	8	Salt Lake City	Utah	B	45.0	D A V	45.0 45.0 27.0	FCC Houdri.	12.0 13.0				5.93
Husky Oil Company	8	North Salt Lake	Utah	B	12.0	D A V	12.0 12.0 3.8	Thermo.	6.9				5.77
Phillips Petro. Company	8	Woods Cross	Utah	B	23.0	D A V	23.0 23.0 3.0	Thermo	10.5			2.2	6.02
Amoco Oil Company	8	Casper	Wym.	D	43.0	A V	43.0 13.5	FCC	11.0	F M N O	1.8 2.6 1.0 0.3	1.55	5.00
Husky Oil Company	8	Cheyenne	Wym.	B	24.6	D A V	24.6 24.6 14.0	FCC	12.5			3.0	7.08
Husky Oil Company	8	Cody	Wym.	B	11.2	D A V	11.2 11.2 6.5	FCC	4.3			4.0	9.17
Little America Ref. Company	8	Casper	Wym.	B	23.0	D A V	23.0 23.0 5.8	Thermo.	10.5			2.0	6.03
Mountaineer Ref. Company Inc.	8	LaBarge	Wym.	A	0.50	A	0.5						1.0
Pasco Inc.	8	Sinclair	Wym.	B	42.0	D A V	42.0 42.0 14.2	FCC	12.8			2.3	4.82
Sage Creek Ref. Company	8	Cowley	Wym.	A	1.2	A	1.2						1.0
Southwestern Ref. Company	8	LaBarge	Wym.	A	0.33	A	0.33						1.0
Tesoro Petro. Corporation	8	Newcastle	Wym.	B	11.0	D A	11.0 11.0	Thermo.	8.0				6.36
Texaco Inc.	8	Casper	Wym.	B	21.0	D A V	21.0 21.0 10.0	Press. Coke FCC	4.0 7.0			1.5	6.48

TABLE 51 cont'd
PETROLEUM REFINERY - PROCESS BREAKDOWN

COMPANY	REGION	LOCATION	STATE	SUBCAT.	REFINERY CAPACITY 1000 bbl/day	CRUDE PROCESSES Process	CRUDE PROCESSES Capacity 1000 bbl/day	CRACKING PROCESSES Process	CRACKING PROCESSES Capacity 1000 bbl/day	LUBE PROCESSES Process	LUBE PROCESSES Capacity 1000 bbl/day	ASPHALT PRODUCTION Capacity 1000 bbl/day	PROCESS CONFIGURATION
Atlanta Richfield Company	9	Carson	Cal.	C	173.0	A V	173.0 93.0	Gas-Oil Cr. Visbreak. Delay. Cok. FCC Hydro.	12.5 42.0 30.0 65.0 19.7				7.41
Beacon Oil Company	9	Hanford	Cal.	B	12.1	A	12.1	Gas-Oil Cr. Visbreak.	0.5 2.75				2.60
Exxon Company USA	9	Benicia	Cal.	B	95.0	D A V	95.0 95.0 53.0	Fluid. Cok. FCC Hydro.	21.6 57.0 22.0				8.91
Fletcher Oil & Ref. Company	9	Carson	Cal.	A	16.2	D A	16.2 16.2						2.0
Golden Bear Div. (Witco)	9	Oildale	Cal.	A	11.0	D A V	11.0 11.0 9.5			Unk.	4.0	3.2	11.09
Gulf Oil Company	9	Santa Fe Springs	Cal.	B	53.8	D A V	53.8 53.8 25.0	Visbreak. FCC Hydro.	13.8 13.8 11.0			4.0	7.66
Mobil Oil Corporation	9	Torrence	Cal.	B	130.0	D A V	100.0 130.0 95.0	Visbreak Delay. Cok. FCC Hydro.	16.0 46.64 56.0 18.0				8.81
Mohawk Petro. Corporation Inc.	9	Bakers-field	Cal.	A	22.8	A	22.8						1.0
Newhall Ref. Company Inc.	9	Newhall	Cal.	A	8.0	A V	8.0 5.0					3.0	6.13
Phillips Petro. Company	9	Avon	Cal.	D	110.0	D A V	90.0 110.0 74.5	Fluid. Cok. FCC Hydro.	42.0 47.0 22.0	Unk.	1.67		8.75
Powerline Oil Company	9	Santa Fe Springs	Cal.	B	30.0	D A V	30.0 30.0 15.0	FCC	12.0			5.0	6.90
Sequoia Ref. Company	9	Hercules	Cal.	B	28.3	D A V	28.3 28.3 5.9	Hydro.	2.9				2.82
Shell Oil Company	9	Martinez	Cal.	E	103.0	D A V	85.0 103.0 55.3	FCC Hydro.	86.0 19.0	A M P	3.5 4.8 1.8	10.4	10.96
Shell Oil Company	9	Wilmington	Cal.	D	101.0	D A V	101.0 101.0 60.0	Delay. Cok. FCC	30.0 40.0	C D E G M	7.8 24.3 1.8 18.6 7.8		14.51

TABLE 51 cont'd
PETROLEUM REFINERY - PROCESS BREAKDOWN

COMPANY	REGION	LOCATION	STATE	SUBCAT.	REFINERY CAPACITY 1000 bbl/day	CRUDE PROCESSES		CRACKING PROCESSES		LUBE PROCESSES		ASPHALT PRODUCTION Capacity 1000 bbl/day	PROCESS CONFIGURATION
						Process	Capacity 1000 bbl/day	Process	Capacity 1000 bbl/day	Process	Capacity 1000 bbl/day		
STD. Oil Company of Calif.	9	Bakers-Field	Cal.	A	26.0	A	26.0					1.1	1.51
STD. Oil Company of Calif.	9	El Segundo	Cal.	C	230.0	D A V	120.0 230.0 103.0	Delay. Cok. FCC Hydro.	54.0 54.5 49.0			8.3	6.51
STD. Oil Company of Calif.	9	Richmond	Cal.	E	190.0	D A V	190.0 190.0 150.0	FCC Hydro.	54.5 67.5	A C G H J Q	3.1 62.4 7.3 6.2 2.9 4.0	11.0	13.21
Texaco Inc.	9	Wilmington	Cal.	B	75.0	D A	22.0 75.0	Delay. Cok. FCC Hydro.	48.0 28.0 20.0				8.97
Union Oil Company of Calif.	9	Los Angeles	Cal.	B	111.0	D A V	86.0 111.0 83.0	Visbreak. FCC Hydro.	20.0 52.0 21.0			10.0	8.63
Union Oil Company of Calif.	9	San Francisco	Cal.	D	115.0	D A V	115.0 115.0 38.5	Delay. Cok. Hydro.	42.5 30.0	D E G H	11.2 5.1 6.1 0.8	6.15	9.34
STD. Oil Company of Calif.	9	Barber's Point	Haw.	B	40.0	D A V	40.0 40.0 15.0	FCC	23.0			1.3	6.19
STD. Oil Company of Calif.	10	Portland	Ore.	A	15.0	A V	15.0 15.0					8.6	8.88
Atlantic Rich-field Company	10	Fernadale	Wash.	B	100.0	D A V	100.0 100.0 55.0	Delay. Cok. Hydro.	29.0 35.0				6.39
Mobil Oil Corporation	10	Ferndale	Wash.	B	74.5	D A V	74.5 74.5 7.0	Visbreak. Thermo.	7.0 27.5				4.87
Shell Oil Company	10	Anacortes	Wash.	B	94.0	D A V	94.0 94.0 33.0	FCC	53.0				5.73

TABLE 52 cont'd
PETROLEUM REFINERY - PROCESS BREAKDOWN

COMPANY	REGION	LOCATION	STATE	SUBCAT.	REFINERY CAPACITY 1000 bbl/day	CRUDE PROCESSES Process	CRUDE PROCESSES Capacity 1000 bbl/day	CRACKING PROCESSES Process	CRACKING PROCESSES Capacity 1000 bbl/day	LUBE PROCESSES Process	LUBE PROCESSES Capacity 1000 bbl/day	ASPHALT PRODUCTION Capacity 1000 bbl/day	PROCESS CONFIG-URATION
Sound Ref. Inc.	10	Tacoma	Wash.	A	4.7	D A V	4.7 4.7 4.5			Unk.	1.9	2.6	14.85
STD. Oil Company of Calif.	10	Richmond Beach	Wash.	A	5.0	A V	5.0 5.0					4.0	11.6
Texaco Inc.	10	Anacortes	Wash.	B	63.0	D A V	63.0 63.0 22.5	FCC	25.0				4.74
U.S. Oil & Ref. Company	10	Tacoma	Wash.	A	16.0	D A V	16.0 16.0 3.2					3.0	4.45
STD. Oil Company of Calif.	10	Kenal	Alka.	A	22.0	D A	22.0 22.0					0.3	2.16
Tesoro-Alaskan Petro. Corp.	10	Kenal	Alka.	A	39.5	D A	39.5 39.5						2.0

SECTION X

BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE -- EFFLUENT LIMITATIONS

The application of best available technology economically achievable is being defined as further reductions of water flows in-plant and the addition of a physical - chemical treatment step (activated carbon), end-of-pipe. The limitations, which set numerical values for the allowable pollutant discharges within each subcategory for BATEA are presented in Tables 1-6. Although there are specific systems which can effectively reduce the water usage from a particular process to nearly zero, these "zero discharge" systems cannot be uniformly applied throughout the refinery to develop "zero discharge" criteria for the entire refinery.

BATEA in-plant technology is based on control practices now practiced by some plants in the petroleum refining industry, and include the following:

(1) Use of air cooling equipment.
(2) Reuse of sour water stripper bottoms in crude desalters.
(3) Reuse of once-through cooling water as make-up to the water treatment plant.
(4) Using waste water treatment plant effluent as cooling water, scrubber water, and influent to the water treatment plant.
(5) Reuse of boiler condensate as boiler feedwater.
(6) Recycle of water from coking operations.
(7) Recycle of waste acids from alkylation units.
(8) Recycle of overhead water in water washes.
(9) Reuse overhead accumulator water in desalters.
(10) Use of closed compressor and pump cooling water system.
(11) Reuse of heated water from the vacuum overhead condensers to heat the crude. This reduces the amount of cooling water needed.
(12) Use of rain runoff as cooling tower make-up or water treatment plant feed.
(13) Other methods.

Flow

Flow reductions proposed for BATEA effluent limitations were derived from further analysis of the 1972 National Petroleum Waste Water Characterization Studies. The flows from refineries in each subcategory meeting the BPCTCA flow basis were averaged to determine the flow basis for establishment of BATEA effluent limitations. That these average flows are achievable within the petroleum refining industry is readily demonstrable, by determining the number and geographical distribution of refineries in the United States currently at, or lower than, the proposed BATEA flows. There are 3 to 5 refineries in each of the five subcategories which have flows less than or equal to the proposed BATEA effluent limitations. These refineries range in size from 827,000 to 69,000,000 cubic meters per stream day (5,200 to 434,000 barrels per stream day), and range in cracking capacity from 0 to 106 percent. The geographical distribution of these refineries indicates that good water practices, and consequently low waste water flows, are not confined to water - short areas or cool climates, but are located throughout the United States. Within this group of refineries with low-water usage, there are refineries located in both high rainfall and dry areas (Washington and New Mexico) and areas of extreme temperatures (New Mexico and Texas to Alaska and Minnesota).

Consequently, these flows, shown in Table 52, were used as the basis for establishment of BATEA effluent limitations. The objective of this basis for flow is to provide inducement for in-plant reduction of both flow and contaminant loadings prior to end-of-pipe treatment. However, it is not the intent of these effluent limitations to specify either the unit waste water flow which must be achieved or the waste water treatment practices which must be employed at the individual petroleum refinery.

The end-of-pipe system proposed for BATEA technology is based on the addition of activated carbon adsorption in fixed bed columns, to the treatment system proposed as BPCTCA technology.

Procedure for Development of BATEA Effluent Limitations

The effluent limitations proposed for BATEA technology are based on refinery pilot plant data, which indicate the percentage reductions achievable or concentrations achievable for effluents from activated carbon adsorption systems. These data are presented in Table 53.

These concentrations were then used in conjunction with the BATEA flows from Table 53 or the percentage reductions were applied to the BPCTCA effluent limit. The daily annual average effluent limitations determined are contained in Table 54.

Since these effluent limitations are based upon pilot plant data, which have not been fully demonstrated in full-scale installations as actual performance data becomes available, the effluent limitations presented in Tables 1-6 may require revision.

Variability Allowance for Treatment Plant Performance

The effluent limitations presented in Tables 1-6 have taken into consideration the variability factors, as in BPCTCA. Since there is not enough performance data from physical - chemical treatment systems available at this time to determine variability, the ratios established for BPCTCA at the 98% confidence level have been used. (See Table 55).

TABLE 52

FLOW BASIS FOR DEVELOPING BATEA EFFLUENT LIMITATIONS

Subcategory	Flow, per unit throughout	
	M3/M3	Gallons/BBL
Topping	0.255	10.5
Cracking	0.33	14
Petrochemical	0.46	19
Lube	0.73	30.5
Integrated	0.88	36.5

TABLE 53

BATEA REDUCTIONS IN POLLUTANT LOADS ACHIEVABLE BY APPLICATION OF ACTIVATED CARBON TO MEDIA FILTRATION EFFLUENT BPCTCA

Parameter	Type of Data	Achievable Refinery Effluent mg/L	Achievable Refinery Effluent % Reduction	References
BOD	Pilot Plant	5	-	21,27,31A,48,62A
COD	Pilot Plant	-	75	21,27,31A,47,53,62A
TOC	Pilot Plant	15	-	17,31A,48,62A
TSS	Pilot Plant	5	-	31A,48,53,62A
Oil	Pilot Plant	1-1.7	80	31A,48,62A
Phenols	Pilot Plant	0.02	99	31A,48,62A
Ammonia	Pilot Plant	-	60	27,31A,62A
Sulfides	No data	-	-	

TABLE 54
BATEA

Annual Average Daily Kilograms of Pollutants/1000 Cubic Meters of Feedstock (1) Per Stream Day
(Annual Average Daily Pounds of Pollutants/1000 BBL of Feedstock Per Stream Day)

Refinery Subcategory	BOD5	COD	TOC	Total Suspended Solids	Oil & Grease	Phenolic Compounds	Ammonia(N)	Sulfide	Total Chromium	Hexavalent Chromium
Topping	1.2(0.44)	5.0(1.75)	3.7(1.3)	1.2(0.44)	0.25(0.088)	0.0051(0.0018)	0.34(0.12)	0.025(0.0087)	0.062(0.022)	0.0012(0.00044)
Cracking	1.6(0.58)	9.6(3.4)	5.0(1.75)	1.6(0.58)	0.34(0.12)	0.0065(0.0023)	2.3 (0.8)	0.034(0.012)	0.082(0.029)	0.0016(0.00058)
Petrochemical	2.2(0.79)	10.8(3.8)	6.8(2.4)	2.2(0.79)	0.45(0.16)	0.0091(0.0032)	2.8 (1.0)	0.045(0.016)	0.11 (0.040)	0.0022(0.00079)
Lube	3.7(1.3)	20.0(6.9)	10.8(3.8)	3.7(1.3)	0.71(0.25)	0.014 (0.0051)	2.8 (1.0)	0.071(0.025)	0.18 (0.063)	0.0037(0.0013)
Integrated	4.2(1.5)	23.7(8.4)	13.0(4.6)	4.2(1.5)	0.85(0.30)	0.017 (0.0061)	2.8 (1.0)	0.085(0.030)	0.22(0.076)	0.0042(0.0015)
Runoff(2)	0.0050(0.042)	0.014(0.12)	0.016(0.13)	0.0050(0.042)	0.0010(0.009)	--	--	--	--	--
Ballast (3)	0.0050(0.042)	0.019(0.16)	0.016(0.13)	0.0050(0.042)	0.0010(0.009)	--	--	--	--	--

(1) Feedstock - Crude oil and/or natural gas liquids.
(2) The additional allocation being allowed for contaminated storm runoff flow, kg/1000 (lb/1000 gallons), shall be based solely on that storm flow which passes through the treatment system. All additional storm runoff, that has been segregated from the main waste stream, shall not exceed a TOC concentration of 35 mg/l or Oil & Grease concentration of 15 mg/l when discharged.
(3) This is an additional allocation, based on ballast water intake - kilograms per 1000 liters (pounds per 1000 gallons).

TABLE 55

VARIABILITY FACTORS BASED ON PROPERLY DESIGNED AND OPERATED WASTE TREATMENT FACILITIES-BATEA

	BOD_5	COD	TOC	TSS	O & G	Phenol	Ammonia	Sulfide	CrT	Cr6
Daily Variability	2.1	2.0	1.6	2.0	2.0	2.4	2.0	2.2	2.0	2.2
30-day Variability	1.7	1.6	1.3	1.7	1.6	1.7	1.5	1.4	1.7	1.4

SECTION XI

NEW SOURCE PERFORMANCE STANDARDS

Recommended effluent limitations for new source performance standards are based upon the application of BPCTCA control technology to the waste water flows used as the basis for BATEA effluent limitations. The proposed BADT effluent limitations are shown in Tables 1-6.

The refining technology available today does not call for major innovations in refining processes. Basically, BADT refining technology consists of the same fundamental processes which are already in practice, with few modifications and additions. However, a major design criterion for new refinery capacity is reuse/ recycle of water streams to the greatest extent possible, in order to minimize discharges to waste water treatment facilities. Consequently, the water flow on which new source performance standards were based is identical to the best available technology economically achievable flow, which reflects the best water usage as demonstrated in the petroleum refining industry. These flows are shown in Table 52.

It should be clearly understood that no recommendations have been made, nor are any implied, regarding the substitution of processes which produce a lower raw waste load for others with higher raw waste load.

This is based on the consideration that the choice of a particular commercial route is governed largely by the availability of feedstocks and on the conditions in the product markets. Companies produce a given mix of products based on their particular marketing and feedstock position within the industry. The substitution of a cleaner process may be possible for new producers from a technical point of view, but completely impossible based on limited availability of the required alternative feedstocks or on the lack of viable markets for new co-products.

The waste water treatment technology recommended for BADT effluent limitations is the same as called for by BPCTCA and does not include physical - chemical treatment, because that technology has not been sufficiently demonstrated by the petroleum refining industry.

Procedure for Development of BADT Effluent Limitations

The effluent limitations proposed for BADT technology are based on the concentrations considered achievable by BPCTCA and the flows from BATEA. The daily annual average effluent limitations thus determined are contained in Table 56.

TABLE 56
BADT

NEW SOURCE PERFORMANCE STANDARDS FOR THE PETROLEUM REFINING INDUSTRY

Annual Daily Kilograms of Pollutants/1000 Cubic Meters of Feedstock (1) Per Stream Day
(Annual Average Daily Pounds of Pollutants/1000 BBL of Feedstock Per Stream Day)

Refinery Subcategory	BOD5	COD	TOC	Total Suspended Solids	Oil & Grease	Phenolic Compounds	Ammonia(N)	Sulfide	Total Chromium	Hexavalent Chromium
Topping	3.7(1.3)	19.8(7.0)	8.2(2.9)	2.5(0.88)	1.2(0.44)	0.025(0.0088)	0.85(0.30)	0.025(0.0088)	0.062(0.022)	0.0012(0.00044)
Cracking	5.1(1.8)	38 (13.4)	11.3(4.0)	3.4(1.2)	1.6(0.58)	0.034(0.012)	5.7 (2.0)	0.034(0.012)	0.082(0.029)	0.0016(0.00058)
Petrochemical	6.8(2.4)	43 (15.2)	15.0(5.3)	4.5(1.6)	2.2(0.79)	0.045(0.016)	7.1 (2.5)	0.045(0.016)	0.11 (0.040)	0.0022(0.00079)
Lube	10.8(3.8)	79 (28.0)	24 (8.4)	7.1(2.5)	3.5(1.25)	0.071(0.025)	7.1 (2.5)	0.071(0.025)	0.18(0.062)	0.0037(0.0013)
Integrated	13.0(4.6)	95 (33.5)	29 (10.1)	8.5(3.0)	4.2(1.5)	0.085(0.030)	7.1 (2.5)	0.085(0.030)	0.22(0.076)	0.0042(0.0015)
Runoff(2)	0.015(0.125)	0.12(1.0)	0.033(0.275)	0.010(0.083)	0.0050(0.042)	--	--	--	--	--
Ballast(3)	0.015(0.125)	0.15(1.25)	0.033(0.275)	0.010(0.083)	0.0050(0.042)	--	--	--	--	--

(1) Feedstock - Crude oil and/or natural gas liquids.
(2) The additional allocation being allowed for contaminated storm runoff flow, kg/1000 liters (lb/1000 gallons), shall be based solely on that storm flow which passes through the treatment system. All additional storm runoff, that has been segregated from the main waste stream, shall not exceed a TOC concentration of 35mg/l or Oil & Grease concentration of 15 mg/l when discharged.
(3) This is an additional allocation, based on ballast water intake - kilograms per 1000 liters (pounds per 1000 gallons).

Variability Allowance for Treatment Plant Performance

The guideline numbers presented in Tables 1-6 have taken into consideration the variability factors, as in BPCTCA. Since the treatment technology and process technology for BADT are the same as BPCTCA, the ratios established for BPCTCA have been used in BADT.

TABLE 57

METRIC UNITS

CONVERSION TABLE

MULTIPLY (ENGLISH UNITS)		by		TO OBTAIN (METRIC UNITS)
ENGLISH UNIT	ABBREVIATION	CONVERSION	ABBREVIATION	METRIC UNIT
acre	ac	0.405	ha	hectares
acre - feet	ac ft	1233.5	cu m	cubic meters
British Thermal Unit	BTU	0.252	kg cal	kilogram - calories
British Thermal Unit/pound	BTU/lb	0.555	kg cal/kg	kilogram calories/kilogram
cubic feet/minute	cfm	0.028	cu m/min	cubic meters/minute
cubic feet/second	cfs	1.7	cu m/min	cubic meters/minute
cubic feet	cu ft	0.028	cu m	cubic meters
cubic feet	cu ft	28.32	l	liters
cubic inches	cu in	16.39	cu cm	cubic centimeters
degree Fahrenheit	F°	0.555(°F-32)*	°C	degree Centigrade
feet	ft	0.3048	m	meters
gallon	gal	3.785	l	liters
gallon/minute	gpm	0.0631	l/sec	liters/second
horsepower	hp	0.7457	kw	killowatts
inches	in	2.54	cm	centimeters
inches of mercury	in Hg	0.03342	atm	atmospheres
pounds	lb	0.454	kg	kilograms
million gallons/day	mgd	3,785	cu m/day	cubic meters/day
mile	mi	1.609	km	kilometer
pound/square inch (gauge)	psig	(0.06805 psig +1)*	atm	atmospheres (absolute)
square feet	sq ft	0.0929	sq m	square meters
square inches	sq in	6.452	sq cm	square centimeters
tons (short)	t	0.907	kkg	metric tons (1000 kilograms)
yard	y	0.9144	m	meters

* Actual conversion, not a multiplier

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SECTION XIII

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SECTION XIV

GLOSSARY AND ABBREVIATIONS

Glossary

Acid Oil

Straight chain and cyclic hydrocarbon with carboxyl group(s) attached.

Act

The Federal Water Pollution Act Amendments of 1972.

Aerobic

In the presence of oxygen.

Alkylates

Branched paraffin hydrocarbons.

Anaerobic

Living or active in absence of free oxygen.

Aquatic Life

All living forms in natural waters, including plants, fish, shellfish, and lower forms of animal life.

Aromatics

Hydrogen compounds involving a 6-carbon, benzene ring structure.

Best Available Technology Economically Achievable (BATEA)

Treatment required by July 1, 1983 for industrial discharge to surface waters as defined by section 310 (b) (2) (A) of the Act.

Best Practicable Control Technology Currently Achievable (BPCTCA)

Treatment required by July 1, 1977 for industrial discharge to surface waters as defined by section 301 (b) (1) (A) of the Act.

Best Available Demonstrated Technology (BADT)

Treatment required for new sources as defined by section 306 of the Act.

Biochemical Oxygen Demand

Oxygen used by bacteria in consuming a waste substance.

Blowdown

A discharge from a system, designed to prevent a buildup of some material, as in boiler and cooling tower to control dissolved solids.

Butadiene

Synthetic hydrocarbon having two unsaturated carbon bonds.

By-Product

Material which, if recovered, would accrue some economic benefit, but not necessarily enough to cover the cost of recovery.

Capital Costs

Financial charges which are computed as the cost of capital times the capital expenditures for pollution control. The cost of capital is based upon a weighted average of the separate costs of debt and equity.

Catalyst

A substance which can change the rate of a chemical reaction, but which is not itself involved in the reaction.

Category and Subcategory

Divisions of a particular industry which processed different traits which affect water quality and treatability.

Chemical Oxygen Demand

Oxygen consumed through chemical oxidation of a waste.

Clarification

The process of removing undissolved materials from a liquid. Specifically, removal of solids either by settling or filtration.

Coke Petroleum

Solid residue of 90 to 95 percent fixed carbon.

Cycles of Concentration

The ratio of the dissolved solids concentration of the recirculating water to make-up water.

Depletion or Loss

The volume of water which is evaporated, embodied in product, or otherwise disposed of in such a way that it is no longer available for reuse in the plant or available for reuse by others outside the plant.

Depreciation

The cost reflecting the deterioration of a capital asset over its useful life.

Direct-Fired Heater

A heater in which heat is supplied by combustion, as distinguished from a heat exchanger where heat is supplied by a hot liquid or gas.

Emulsion

A liquid system in which one liquid is finely dispersed in another liquid in such a manner that the two will not separate through the action of gravity alone.

End-of-Pipe Treatment

Treatment of overall refinery wastes, as distinguished from treatment at individual processing units.

Filtration

Removal of solid particles or liquids from other liquids or gas streams by passing the liquid or gas stream through a filter media.

Fractionator

A generally cylindrical tower in which a mixture of liquid components is vaporized and the components separated by carefully varying the temperature and sometimes pressure along the length of the tower.

Gasoline

A mixture of hydrocarbon compounds with a boiling range between 100o and 400o F.

Grease

A solid or semi-solid composition made up of animal fats, alkali, water, oil and various additives.

Hydrocarbon

A compound consisting of carbon and hydrogen.

Hydrogenation

The contacting of unsaturated or impure hydrocarbons with hydrogen gas at controlled temperatures and pressures for the purpose of obtaining saturated hydrocarbons and/or removing various impurities such as sulfur and nitrogen.

Industrial Waste

All wastes streams within a plant. Included are contact and non-contact waters. Not included are wastes typically considered to be sanitary wastes.

Investment Costs

The capital expenditures required to bring the treatment or control technology into operation. These include the traditional expenditures such as design; purchase of land and materials; site preparation; construction and installation; etc., plus any additional expenses required to bring the technology into operation including expenditures to establish related necessary solid waste disposal.

Isomer

A chemical compound that has the same number, and kinds of atoms as another compound, but a different structural arrangement of the atoms.

Mercaptan

An organic compound containing hydrogen, carbon, and sulfur (RSH).

Microcrystalline Wax

A non-crystalline solid hydrogen with a melting point of about 106o to 195o F. Also known as petrolatum.

Motor Octane Number

An expression of the antiknock value of gasoline.

Naphtha

A petroleum fraction, including parts of the boiling range of gasoline and kerosene, from which solvents are obtained.

Naphthenic Acids

Partially oxidized naphthalenes.

New Source

Any building, structure, facility, or installation from which there is or may be a discharge of pollutants and whose construction is commenced after the publication of the proposed regulations.

No Discharge of Pollutants

No net increase (or detectable gross concentration if the situation dictates) of any parameter designated as a pollutant to the accuracy that can be determined from the designated analytical method.

Octane

The numerical rating of a gasoline's resistance to engine knock.

Olefins

Unsaturated straight-chain hydrocarbon compounds seldom present in crude oil, but frequently in cracking processes.

Operation and Maintenance

Costs required to operate and maintain pollution abatement equipment. They include labor, material, insurance, taxes, solid waste disposal, etc.

Overhead Accumulator

A tank in which the condensed vapors from the tops of the fractionators, steam strippers, or stabilizers are collected.

Paraffin Wax

A crystalline solid hydrocarbon with a melting point of 105o to 155o F.

Petroleum

A complex liquid mixture of hydrocarbons and small quantities of nitrogen, sulfur, and oxygen.

pH

A measure of the relative acidity or alkalinity of water. A pH of 7.0 indicates a neutral condition. A greater pH indicates alkalinity and a lower pH indicates acidity. A one unit change in pH indicates 10 fold change in acidity and alkalinity.

Phenol

Class of cyclic organic derivatives with basic formula C6HOH.

Pretreatment

Treatment proved prior to discharge to a publicly owned treatment works.

Process Effluent or Discharge

The volume of water emerging from a particular use in the plant.

Plant Effluent or Discharge After Treatment

The volume of waste water discharge from the industrial plant. In this definition, any waste treatment device is considered part of the industrial plant.

Raffinate

The portion of the oil which remains undissolved and is not removed by solvent extraction.

Raw

Untreated or unprocessed.

Reduced Crude

The thick, dark, high-boiling residue remaining after crude oil has undergone atmospheric and/or vacuum fractionation.

Secondary Treatment

Biological treatment provided beyond primary clarification.

Sludge

The settled solids from a thickener or clarifier. Generally, almost any flocculated settled mass.

Sour

Denotes the presence of sulfur compounds, such as sulfides and mercaptans, that cause bad odors.

Spent Caustic

Aqueous solution of sodium hydroxide that has been used to remove sulfides, mercaptans, and organic acids from petroleum fractions.

Stabilizer

A type of fractionator used to remove dissolved gaseous hydrocarbons from liquid hydrocarbon products.

Standard Raw Waste Loads (SRWL)

Net pollution loading produced per unit of production (or raw material) by a refining process after separation of the separables (STS).

Stripper

A unit in which certain components are removed from a liquid hydrocarbon mixture by passing a gas, usually steam, through the mixture.

Supernatant

The layer floating above the surface of a layer of solids.

Surface Waters

Navigable waters. The waters of the United States, including the territorial seas.

Sweet

Denotes the absence of odor-causing sulfur compounds, such as sulfides and mercaptans.

Topping Plant

A refinery whose processing is largely confined to oil into raw products by simple atmospheric distillation.

Total Suspended Solids (TSS)

Any solids found in waste water or in the stream which in most cases can be removed by filtration. The origin of suspended matter may be man-made wastes or natural sources such as silt from erosion.

Waste Discharged

The amount (usually expressed as weight) of some residual substance which is suspected or dissolved in the plant effluent after treatment if any.

Waste Generated

The amount (usually expressed as weight) of some residual substance generated by a plant process or the plant as whole and which is suspended or dissolved in water. This quantity is measured before treatment.

Waste Loading

Total amount of pollutant substance, generally expressed as pounds per day.

Abbreviations

AL - Aerated Lagoon

AS - Activated Sludge

API - American Petroleum Institute

BADT - Best Available Demonstrated Technology

BATEA - Best Available Technology Economically Achievable

BPCTCA - Best Practicable Control Technology Currently Available

bbl - Barrel

BOD - Biochemical Oxygen Demand

bpcd - Barrels per calendar day

bpsd - Barrels per stream day (operating day)

BS and W - Bottom Sediment and Water

BTX - Benzene-Toluene-Xylene mixture

COD - Chemical Oxygen Demand

cu m - cubic meter(s)

DAF - Dissolved Air Flotation

DO - Dissolved Oxygen

gpm - Gallons per minute

k - thousand(e.g., thousand cubic meters)

kg - kilogram(s)

l - liter

lb - pound(s)

LPG - Liquified Petroleum Gas

M - Thousand (e.g., thousand barrels)

MBCD - Thousand Barrels per calendar day

MBSD - Thousand Barrels per stream day

mgd - Million gallons per day

mg/L - Milligrams per liter (parts per million)

MM - Million (e.g., million pounds)

PP - Polishing pond

psig - pounds per square inch, gauge (above 14.7 psig)

RSH - Mercaptan

sec - Second-unit of time

scf - Standard cubic feet of gas at 60o F and 14.7 psig

SIC - Standard Industrial Classification

SRWL - Standard Raw Waste Load

SS - Suspended Solids

STS - Susceptible to Separation

TOC - Total Organic Carbon

TSS - Total Suspended Solids

VSS - Volatile Suspended Solids

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